a good bunsen flame and then for about half an hour in a blowpipe flame.

When cold, the solid cake is placed in a porcelain dish, the crucible being washed first with water and then with hydrochloric acid, the latter being then gradually added until the ferric and magnesium oxides are completely dissolved (10 grams of the mixture require about 45 c.c. of HCl of D 1·12). The liquid is afterwards evaporated to dryness and treated further as in the preceding method.

**2. Determination of the Carbon.**—With products not attacked by acids, the carbon should be estimated by direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Manganese.**—(*a*) The hydrochloric acid solution obtained in the determination of the silicon as under 1, *a* or 1, *b* is placed in a measuring flask. The residue remaining after treatment of the silica with hydrofluoric and sulphuric acids is dissolved in hydrochloric acid or, if insoluble matter then remains, fused with sodium carbonate and the fused mass dissolved in hydrochloric acid. This solution is added to the other in the measuring flask, the whole made up to volume and the manganese titrated by Volhard's method (*see* Ferro-manganese).

(*b*) In presence of chromium or vanadium, 0·2–2 grams of the sample are fused with a mixture of sodium carbonate and magnesium oxide (*see* 1, *b*) and the product lixiviated with hot water (if the mass is green owing to the presence of manganates, these are reduced by addition of a small quantity of sodium peroxide, excess of which is decomposed by boiling for some time). The residue is collected on a filter, washed with hot water, dissolved in conc. hydrochloric acid, boiled to expel chlorine, and, when cool, made up to volume in a 250 c.c. measuring flask: in an aliquot part the manganese is estimated by Volhard's method (*see* Ferro-manganese).

**4. Determination of the Phosphorus.**—(*a*) An aliquot part of the hydrochloric acid solution obtained after elimination of the silica (*see* 1, *a* and *b*) is concentrated to a syrup and the phosphorus precipitated with the molybdate reagent (*see* Determination of phosphorus in iron).

(*b*) 1-3 grams of the sample are fused with the sodium carbonate-magnesia mixture (*see* 1, *b*), the product being dissolved in hydrochloric acid and the silica rendered insoluble and removed. The solution is then evaporated to dryness, the residue dissolved in nitric acid and the phosphoric acid precipitated with the molybdate reagent.

**5. Determination of the Sulphur.**—1-3 grams of the sample are fused with sodium carbonate and magnesia (*see* 1, *b*), the mass taken up in bromine water, the bromine expelled by boiling, hydrochloric acid added to dissolve the ferric oxide and magnesia, the silica rendered insoluble, the residue taken up in dilute hydrochloric acid and the silica having been

, sulphur and, sometimes, calcium. Phosphorus is an injurious con-
e maximum allowable limit being 0·15–0·2%. The mean percentage
ns of the commoner commercial forms are (Geiger) :

TABLE XV

Compositions of Ferro-silicons

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| . . . . | 25·89 | 29·66 | 51·80 | 53·75 | 51·20 | 75·67 |
| . . . . | 72·92 | 72·99 | 47·30 | 45·09 | 48·89 | 23·01 |
| . . . . | 0·52 | — | 0·30 | 0·11 | — | 0·31 |
| . . . . | 0·42 | 0·56 | 0·35 | 0·11 | 0·37 | 0·26 |
| . . . . | 0·03 | 0·01 | 0·02 | 0·005 | 0·007 | 0·01 |
| . . . . | 0·04 | 0·30 | 0·04 | 0·041 | 0·04 | 0·04 |
| . . . . | — | 0·30 | — | 0·60 | 0·17 | — |
| . . . . | — | 0·25 | — | — | — | — |
| . . . . | — | — | — | 0·04 | — | — |
| . . . . | — | — | — | 0·05 | 0·21 | — |

## ERRO-MANGANESE AND SPIEGELEISEN

nanganese is usually obtained in the blast furnace from a mixture
d manganese minerals, and serves for the de-oxidation of steels
e preparation of manganese steels and other special alloys. It
yellowish white, compact and with a granular structure inter-
pecially in the high percentage types, by bluish, iridescent,
ystals.

*eisen* is a form of white cast-iron very rich in manganese with
lamellar structure and a shining and sometimes iridescent surface ;
same uses as ferro-manganese.

is of these products may include, besides the determination of
nese, also those of the carbon, silicon, phosphorus, sulphur, etc.,
always present in the commercial products in larger or smaller

**ermination of the Manganese.**—Numerous methods, gravi-
lumetric and electrolytic, have been proposed for the determina-
e manganese in ferro-manganese and manganiferous cast-irons
The following will be described : Volhard's volumetric method
recent modifications introduced by Wolff, Schöffel and Donath,
lectrolytic method.

3·2 grams of the pure salt in boiled distilled water and making up to 1 litre.

(2) Sodium arsenite solution, obtained by dissolving 1·6 gram of pure arsenious anhydride and 0·8 gram of pure sodium hydroxide in water, heating if necessary, and making up to 1 litre: 1 c.c. of this solution corresponds with about 0·5 c.c. of the permanganate solution.

*Titration of the permanganate solution* (Sörensen). About 0·3 gram of pure sodium oxalate, in minute crystals and dried at 100°, is weighed exactly, dissolved in 500–600 c.c. of boiling water, mixed with 50 c.c. of dilute sulphuric acid (1 vol. acid to 5 vols. water) and the permanganate solution run in from a burette until a faint pink colour persists. Since 670 grams of sodium oxalate are equivalent, as regards permanganate, to 164·79 grams of manganese as salt, the amount of manganese, $x$, corresponding with the permanganate used is given by

$$670{\cdot}0 : 164{\cdot}79 :: P : x,$$

where $P$ is the quantity of the oxalate taken. The quotient of $x$ by the number of c.c. of permanganate used gives the amount of manganese corresponding with 1 c.c. of permanganate.[1]

*Procedure.* 1–2 grams of ferro-manganese or 2–5 grams of spiegeleisen are treated with nitric acid (D = 1·18) according to the conditions described under 2 (p. 172). The solution is evaporated, ignited to decompose the nitrates, taken up in hydrochloric acid and the silica rendered insoluble, filtered and, if required, weighed. The hydrochloric acid solution, containing the manganese, when cold is made up to 250 or 500 c.c. in a measuring flask. The titration of the manganese is carried out on aliquot parts of the solution, each containing 0·04–0·08 gram of manganese.

If the sample is of high manganese content and hence contains too little iron, it is well to add to each portion 5–10 c.c. of ferric chloride solution (500 grams of pure ferric chloride dissolved in water acidified with hydrochloric acid and the volume made up to 1 litre). In this case it is necessary to ascertain, by a blank test under similar conditions, whether the ferric chloride absorbs permanganate and, if so, to allow for this in the calculation.

*Preliminary test.* Before titrating, a trial test must be made to establish the quantity of permanganate to be added.

An aliquot part of the solution is treated in a litre flask with a few drops of 30% hydrogen peroxide to oxidise any trace of ferrous salt and then heated to boiling to expel the excess of the oxidising agent. After 10–15 minutes' boiling, the volume is made up to 600–700 c.c. with boiling water, a suspension of zinc oxide[2] in water being then added in small amounts and with shaking until all the iron is precipitated in brown flocks (not pale

---

[1] The reaction between sodium oxalate and permanganate takes place thus:

: liquid appears colourless.[1] The precipitate settles rapidly if held inclined in a suitable stand.

ıe precipitate has deposited, 10 c.c. of the permanganate soluded, the liquid shaken, the precipitate allowed to settle and, if tant liquid is colourless, a further 10 c.c. of permanganate are procedure being continued until the liquid contains excess of :. The excess of permanganate is titrated with the sodium ution, which is added gradually and with shaking and with an ter each addition until the liquid is decolorised. From the permanganate used, less that corresponding with the arsenite ded (1 c.c. of arsenite = about 0·5 c.c. of permanganate), the permanganate required to oxidise the manganese completely d approximately.

ı. For the actual titration of the manganese, an aliquot part d equal to that used in the preliminary test is oxidised with eroxide, boiled, diluted with boiling water to 600–700 c.c. and added to precipitate the iron.

he precipitate is settling, the volume of permanganate found us 3–4 c.c. is introduced into a beaker and then rapidly poured sk, the latter being shaken and the beaker rinsed out with water k. When the precipitate has settled again, the excess of peradded is determined by titration with the sodium arsenite as inary test. Next, in order to determine the true titre of the h respect to the permanganate under the exact conditions used, olume of 5 c.c. of the permanganate is added and the liquid lorised by the arsenite solution. From these data a simple gives the amount of permanganate required for the complete f the manganese, and hence the amount of the latter.

vays advisable to carry out control determinations on different s of the solution.

LE. 1 c.c. of the permanganate solution is found to correspond 5 gram of manganese. In the actual test, 35 c.c. of permanganate and the excess required 8 c.c. of arsenite solution, of which 9 c.c. with 5 c.c. of permanganate. Since

$$9 : 5 = 8 : 4{\cdot}44,$$

of permanganate reduced will be 35–4·44 = 30·56 c.c. and 30·56 = amount of manganese in the aliquot part of the solution taken.

s method is used more especially in laboratories where estimations se are made regularly; it is fairly exact and, the solutions being rapid. It cannot be used directly in presence of chromium, vancobalt, these also reducing the permanganate (for the determination titration : the permanganate solution is added little by little to the boiling liquid and the precipitate allowed to settle after each addition, this being continued until the supernatant liquid exhibits a persistent pink colour. In this case, also, a preliminary trial titration is, of course, necessary. It appears, however, that under these conditions, intermediate oxides of manganese may be formed, so that the results are not always exact.

(*b*) ELECTROLYTIC DETERMINATION.[1]—1·5 gram of the finely powdered alloy is treated, in a covered porcelain beaker of about 100 c.c. capacity, with 30 c.c. of nitric acid (D 1·2) containing a few drops of hydrochloric acid. At the end of the action, the clock-glass and the edges of the beaker are washed with water, 1–2 grams of ammonium nitrate added and the liquid evaporated on a water-bath to a syrup and then carefully over a small direct flame to redness.

When cold, the oxides of iron and manganese are dissolved in 4–5 c.c. of conc. hydrochloric acid in the hot, 10 c.c. of 50% sulphuric acid being added to the cooled liquid and the solution heated on a sand-bath until the hydrochloric acid is completely expelled and copious white fumes appear. After being heated with water to dissolve the sulphates of iron and manganese, the liquid is filtered and the filtrate collected in a 250 c.c. measuring flask and the beaker and filter washed repeatedly with boiling water acidified with sulphuric acid.

The filter then contains the silica, contaminated by small quantities of graphitic carbon. If the silicon content is required, the procedure given on p. 171 is followed.

The liquid in the flask is made up to 250 c.c. and 50 c.c. (= 0·3 gram of the alloy)[2] treated in a 100 c.c. beaker with ammonia until the iron begins to precipitate. The liquid is then heated on a steam-bath and dilute sulphuric acid added drop by drop until the ferric hydroxide is completely dissolved. The solution of ferric and manganese sulphates is then poured into a solution of 6–7 grams of ammonium oxalate in a little boiling water contained in an electrolytic cell (not too narrow), 5–6 c.c. of 2% hydrazine sulphate solution being added and the liquid diluted to 200 c.c. and subjected to electrolysis to deposit the iron : $ND_{100} = 0{\cdot}7$ amp., voltage = 4–4·5, duration = 3–5 hours, Winkler electrodes (*see* later : Electrolytic analysis of metals).

When the electrolysis has commenced, 2% hydrazine sulphate solution is allowed to drop in the neighbourhood of the anode from a small tap-funnel drawn out to a capillary (8–10 drops per minute), this addition being continued uninterruptedly throughout the electrolysis.

As soon as the liquid loses its yellow tint and becomes completely colourless, a drop is removed, treated with a drop of dilute nitric acid, 2–3 c.c.

ed by the decomposition of the ammonium oxalate, to redissolve
ese dioxide, and to reduce the volume to 60–70 c.c. The liquid ed with 1·5 gram of chrome alum and 10 grams of ammonium the hot solution filtered directly into the matte Classen capsule. of ammonia (D 0·94) have been added, the liquid is mixed, 70–80° and subjected to electrolysis, the capsule being con- the positive pole. $ND_{100} = 0{\cdot}5\text{–}0{\cdot}6$ amp., voltage = 2–3, = 70–80°, duration = about 2 hours.

e deposition is found to be complete by raising slightly the liquid, the disc functioning as cathode is lifted out and the the dish poured away, the deposited manganese dioxide being ashed with water. The dish is then dried at 100° and heated ed heat to transform the dioxide and the higher oxides into the , $Mn_3O_4$.

old, the dish is washed once more with water to remove any d which may be included, again ignited and weighed rapidly the manganese oxide from absorbing moisture : $Mn_3O_4 \times 0{\cdot}7205$

trolytic method certainly takes longer than the volumetric method, advantage of not requiring standard solutions and of being applicable ence of chromium, cobalt, nickel and vanadium.

**rmination of the Carbon.**—This is usually carried out by the hod (*see* Iron, 1, *a*) or, better, by direct combustion in a current (*see* Iron, 1, *b*).

**rmination of the Silicon.**—When this is required, it may be g with the determination of the manganese (*see* Determination n iron, 2, *b*).

**rmination of the Phosphorus, Sulphur and Arsenic.**— nts are estimated as in cast- or wrought-iron.

⁂

ganese content of ferro-manganeses may vary from 25 to 85% and content from 5 to 7·5%, the two generally increasing together. aneses contain also 0·5–2·5% of silicon, small quantities of phosphorus and minimal traces of sulphur, copper, etc.

isen contains 0·2–1·2% of silicon, 4–5% of carbon and 5–25% of and sometimes, as impurities, small proportions of phosphorus and

# SILICON FERRO-MANGANESE

## (Silico-spiegeleisen)

Silicon ferro-manganese may be regarded as a product intermedi ferro-silicon and ferro-manganese. It is obtained in the blast furn the electric furnace, the latter yielding especially pure product analysis includes the following :

**1. Determination of the Silicon.**—As silicon ferro-mangan attacked either not at all or with difficulty by acids, the silicon sho estimated by the methods given for the determination of silicon in silicon.

**2. Determination of the Manganese.**—As in ferro-silicon.

**3. Determination of the Carbon.**—By direct combustion in a c of oxygen (*see* Iron, 1, *b*).

**4. Determination of the Phosphorus and Sulphur.**—As in silicon.

⁂

Silicon ferro-manganese obtained from the blast furnace contains 20% Mn, 10–12% Si (occasionally 20%), 2–2·5% C, 0·01–0·2% P, and times minimal traces of sulphur.

That from the electric furnace may contain 35–75% Mn, 20–35% Si, 0·6 C, 0·01–0·06% P, 0·02–0·03% S, and sometimes traces of copper, aluminiu

# FERRO-CHROME

Ferro-chrome may be prepared in the blast furnace or the e furnace and serves for making chrome steels. Its analysis includes

**1. Determination of the Chromium.**—The sample is best att by the following methods.[1]

(*a*) Fusion with Sodium Hydroxide and Peroxide. 0·3–0·5 gr the very finely powdered sample are mixed, in a silver crucible or dis with a silver spatula, with 2 grams of sodium hydroxide in minute ments, the mixture being covered with 4 grams of sodium peroxid heated to incipient fusion, the flame being then removed to preven reaction from becoming too violent ; the heat developed in the rea rapidly melts all the contents of the dish or crucible. A little more so peroxide is added to the fused mass, the latter being heated gradua fusion when the reaction begins to abate. After about 10 minutes, 5 grams of sodium peroxide are mixed in and the mass heated rather energetically so as to maintain it in a state of quiet fusion for 20–30 mi should then be completely attacked.

ON WITH SODIUM CARBONATE AND MAGNESIA. 0·3–0·5 gram of owdered sample is mixed with about 10 parts of a mixture arbonate and magnesium oxide, and the mixture heated in a ucible under the conditions prescribed for the analysis of (1, *b*).

*of the chromium.* The fused mass obtained by one of the above lixiviated with water, as indicated on p. 183 (Chrome Steels), ates formed being reduced with sodium peroxide, the liquid ed to expel excess of sodium peroxide and made up to volume measuring flask ; the chromium is then titrated iodometrically 0 or 100 c.c. portions (*see* Chrome Steel).

spected that the attack of the metal has not been completed, the the lixiviation is dried, fused with sodium carbonate and the fused xiviated, the resultant solution being added to that from the first

**mination of the Carbon.**—This is effected by direct com- current of oxygen (*see* Iron, 1, *b*).

**mination of the Manganese.**—The residue obtained in the vith water of the fused mass is dissolved in hydrochloric acid as indicated under Ferro-silicon, 3.

**mination of the Silicon, Phosphorus and Sulphur.**—As on.

⁂

ome contains 40–65% Cr (rarely 80%), quantities of carbon vary- g to the degree of refining, and the ordinary impurities found in Three grades are distinguished commercially :

d ferro-chrome No. 1 (0·3–0·75% C, 60% Cr).
d ferro-chrome No. 2 (1–2% C, 60% Cr).
ry ferro-chrome (4–10% C, 60% Cr).

wing table gives the mean compositions of various ferro-chromes

TABLE XVI

## Composition of Ferro-chromes

| e. | Cr | Fe | C | Si | Al | Mn | Ca | S | P |
|---|---|---|---|---|---|---|---|---|---|
| rbon . | 54·50 | 22·00 | 9· 0 | 2·25 | 0·80 | 0·15 | 0·25 | 0·04 | 0·03 |

## FERRO-TUNGSTEN

Ferro-tungsten is obtained by the direct reduction of natural wol or scheelite with carbon in a crucible, or in the blast furnace or the furnace, and serves for the preparation of tungsten steels.

Ferro-tungsten and steels with high tungsten contents (20%) soluble or difficultly soluble in acids, and to attack them it is neces fuse with alkali. Their analysis includes:

**1. Determination of the Tungsten.**—0·5–2 grams of the fine dered sample are fused with 10 parts of the mixture of sodium ca and magnesia, as under Ferro-silicon, 1 *b*, or 1 gram of the sample fused with 4–5 grams of sodium-potassium carbonate and 0·5 g potassium nitrate. In either case, the product is lixiviated with ho sodium peroxide being added and the liquid boiled to destroy the of this reagent, if the solution appears greenish owing to the pres manganates. The liquid, which contains the tungsten as sodium tu is filtered into a 500 c.c. measuring flask and the residue repeatedly dried and again fused with sodium carbonate, the mass being lixivi recover any small amount of tungsten which may have resisted t attack.

An aliquot part (50 or 100 c.c.) of the total solution is acidifi hydrochloric acid, evaporated to dryness, heated at 135°, taken u in hydrochloric acid, etc., as described for the analysis of tungste

**2. Determination of the Carbon.**—With products insoluble direct oxidation in a current of oxygen must be employed (*see* Iron

**3. Determination of the Silicon.**—The procedure employe ferro-silicon is followed, but since tungstic acid separates with th the latter is treated with hydrofluoric acid and estimated by the weight (*see* Tungsten Steels).

**4. Determination of the Manganese.**—This is carried out residue remaining undissolved when the fused mass is lixiviated wit (*see* Ferro-silicon, 3).

**5. Determination of the Phosphorus and Sulphur.**—As i silicon (*see* p. 196).

⁂

Crucible ferro-tungsten contains, on the average, 25–30% W, 60– 1–1·5% C, with traces of manganese, phosphorus, etc.; that from t furnace always contains considerable proportions of manganese (in som up to 40%) and carbon (4–5%).

Ferro-tungsten obtained in the electric furnace usually has a high t content (80–90% W, 10–2 % Fe, very small amounts of carbon, sili

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 23·29 | 1·75 | 0·33 | 0·80 | 0·06 | — | 0·01 | 0·01 |
| — | 1·36 | 0·33 | 0·43 | 0·09 | Trace | 0·01 | 0·007 |
| — | 0·38 | 0·13 | — | — | Trace | 0·07 | 0·009 |
| 22·0 | — | 0·3 | 0·8 | — | — | 0·01 | 0·02 |
| 15·72 | 0·52 | 0·13 | — | — | — | 0·01 | 0·01 |

## FERRO-VANADIUM

adium is obtained exclusively by electro-thermal processes, n combination with alumino-thermal processes, from mixtures de and vanadium oxide. They serve as deoxidising agents g of cast-iron and steels, and for the preparation of vanadium

ed to-day it is comparatively pure and, besides iron and vana- contains only small quantities of carbon and silicon and some- of phosphorus and manganese. Its analysis includes :

**mination of the Vanadium.**—1–2 grams of the sample are small porcelain dish with nitric acid (D 1·18), evaporated to ined and the oxides obtained fused with sodium peroxide, being extracted with water as indicated in the analysis of eels.[1]

ds from the lixiviation are together made up to 500 c.c. and n in an aliquot part determined as with vanadium steel.

**mination of the Carbon and Silicon.**—As in ordinary cast-

**mination of the Phosphorus.**—This is carried out on an of the 500 c.c. (*see* 1, above) by the method given for estimating n presence of vanadium (*see* Iron, 4, 3).

**mination of the Manganese.**—As in ferro-silicon.

⁂

types of ferro-vanadium contain 35–55% of vanadium, with ies of silicon (0·09–1·2%) and carbon (1–3%) and traces of phos- ur, magnesium and aluminium.

compositions of ferro-vanadiums made in the electric furnace are onini) :

---

nple can be finely powdered, it may be fused at once with a mixture of e and magnesia (*see* p. 195), the mass obtained being lixiviated with

### Compositions of Ferro-vanadium

| No. | V | Fe | C | Si | Al | Mn | Cu | S |
|---|---|---|---|---|---|---|---|---|
| 1 | 55·0 | 40·00 | 4·00 | 0·30 | 0·10 | 0·30 | — | 0·03 |
| 2 | 52·8 | 45·84 | 1·04 | 0·09 | — | — | — | 0·025 |
| 3 | 47·4 | 51·20 | 1·07 | 0·09 | — | 0·07 | 0·01 | 0·009 |
| 4 | 34·1 | 64·22 | 1·42 | 0·12 | 0·12 | 0·12 | — | 0·03 |

## FERRO-MOLYBDENUM

This is obtained industrially by electro-thermal processes and i essentially, together with chromo-molybdenum and molybdenu making molybdenum steels. The elements commonly estimat molybdenum, carbon, silicon, manganese, phosphorus, sulphur and tu

**1. Determination of the Molybdenum.**—1–2 grams of the powdered sample are heated at not too high a temperature with ab parts of the sodium carbonate and magnesia mixture, the semi-fuse being extracted with hot water; these operations are then repea extract any small quantities of molybdenum remaining in the resid Chrome Steels). The two solutions together are made up to 500 c. measuring flask and the molybdenum in an aliquot part (50–10 determined as in molybdenum steels.

**2. Determination of the Carbon.**—By direct combustion in a of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Silicon, Manganese, Phosphoru Sulphur.**—As in ferro-silicon.

**4. Determination of the Tungsten.**—In an aliquot part of t c.c. of solution (*see* 1, above) the tungsten is determined as in ferro-tu

⁂

According to the character of the original ores, different types o molybdenum are obtained. These may contain 15–80% of molyb (usually 50–70%), from 0·5% (for the more refined products) to 5% of 0·1–0·5% of silicon and small quantities of manganese, sulphur, phos and sometimes tungsten.

The commoner commercial products have the following mean comp (Guillet):

TABLE XIX

**Compositions of Ferro-molybdenum**

nium is prepared by electro-thermal and alumino-thermal
m rutile and from iron ores rich in titanium, and serves as a
.gent in the refining of cast-iron and steel.

**mination of the Titanium.**[1]—0·5 gram of the finely powdered
ated in a platinum crucible and, after cooling, evaporated to
a few c.c. of hydrofluoric acid. The residue is then heated
ne in the same crucible with 5–7 grams of potassium bisulphate,
ass taken up in hydrochloric acid (not too dilute) and heated
-bath until solution is complete. The liquid is made up to
, mixed with 20–30 c.c. of concentrated sodium bisulphite
heated gently to reduce the iron to ferrous salts (a drop of
should give no appreciable colour with thiocyanate). When
is complete and the temperature of the liquid not above
addition is made, in one quantity and with shaking, of 70–
ncentrated ammonia containing in solution 30 grams of potas-
. The solution is then heated rapidly and kept near to the
until the precipitate appears white and the supernatant liquid
a greenish-yellow coloration. When cold, the liquid is filtered
cipitate washed, first with ammoniacal ammonium sulphite
then with hot water. The moist precipitate is dissolved in
ydrochloric acid and the titanium oxide in the clear solution
by fresh addition of ammonia. The precipitate is filtered,
ted strongly and weighed: $TiO_2 \times 0{\cdot}6005 = Ti$.
uminium occurs along with the titanium, the oxides thus
fused with bisulphate, the fused mass dissolved in hydro-
and the titanium separated from the aluminium by means of

**mination of the Carbon.**—By direct combustion in a current
(*see* Iron, 1, *b*).

**mination of the Silicon.**—0·3–1 gram is disintegrated with
of sodium carbonate and magnesia (*see* Ferro-silicon, 1, *b*, p.
cold, the semi-fused mass is moistened with water, ground
nd poured into a beaker, the least possible quantity of rinsing
used. The liquid is strongly acidified with hydrochloric acid
ing avoided—left for 1–2 hours and then heated on a water-
e liquid becomes perfectly clear. The solution is evaporated
of sulphuric acid, heated until copious white fumes appear,
cold and the separated silicon filtered off (*see* Ferro-silicon, 1, *b*).

**mination of the Manganese, Phosphorus and Sulphur.**—
ilicon.

The compositions of some of the commoner ferro-titaniums are as follow

### Table XX

### Composition of Ferro-titanium

| No. | Fe | Ti | C | Si | Al | Mn | S |
|---|---|---|---|---|---|---|---|
| 1 | 36·85 | 56·63 | 4·62 | 1·25 | 0·44 | 0·10 | 0·045 |
| 2 | 78·54 | 18·37 | 0·67 | 1·40 | 0·69 | 0·18 | 0·074 |
| 3 | 87·68 | 11·21 | 0·67 | 0·37 | — | — | 0·03 |

## FERRO-ALUMINIUM

Ferro-aluminium is usually prepared in the electric furnace by re alumina in presence of iron, and serves, like metallic aluminium— is much more used at the present time—as a deoxidising agent in the r of cast-iron and steel. Its analysis includes :

**1. Determination of the Aluminium.**—Exact determination aluminium necessitates preliminary expulsion of the iron by exha with ether in Rothe's apparatus, the aluminium being then precipita phosphate.[1] When, however, very exact determination is not rec the following more rapid method (Regelsberger's) may be followed

5 grams of the coarsely powdered sample are dissolved in a por dish in dilute sulphuric acid (1 : 4), evaporated to dryness and hea a sand-bath until white fumes are emitted. When cold the sulphat dissolved in hot water and the solution poured into a 300 c.c. mea flask, cooled, made up to volume, and filtered through a dry pleated into a dry vessel.

To 100 c.c. of the filtrate sodium bisulphite or hyposulphite is until the iron is completely reduced (a drop of the liquid should gi colour with thiocyanate), the liquid cooled, most of the free acid neut with sodium carbonate, and the solution poured into a boiling m of 50 c.c. of sodium hydroxide solution (containing 10 grams of s hydroxide) with 40 c.c. of potassium cyanide solution (containing 8 of potassium cyanide).[2] When cold, the liquid is introduced into c.c. measuring flask, made up to volume, and filtered through a dry To 300 c.c. of the filtrate (= 1 gram of the alloy), concentrated ammo nitrate solution (15 grams in a little water) is added, the liquid being to expel most of the ammonia, and the precipitated aluminium hydr filtered off, washed until the washing water no longer gives a blue colo m, and titrated with permanganate ; the corresponding amount de is deducted from the total weight of the alumina.

**rmination of the Carbon, Silicon, Manganese, Phosphorus ur.**—As with iron (*see* p. 163).

usual types of ferro-aluminium contain 10–20 % of aluminium.

## LECTROLYTIC ANALYSIS OF METALS

by the electrolytic method has now reached a high degree o nd forms a valuable aid in the examination of metals and alloys eir accuracy, their simplicity and their neatness, electrolytic l be given the preference over other methods, and a brief descrip- ecessary apparatus and a short outline of the conditions to be the various operations will now be given.

**ces of Current.**—The continuous current used should not be but must be as far as possible constant. It may be obtained *ary batteries*, *accumulators*, or the *street mains*.

batteries do not answer very well the requirements of elec-

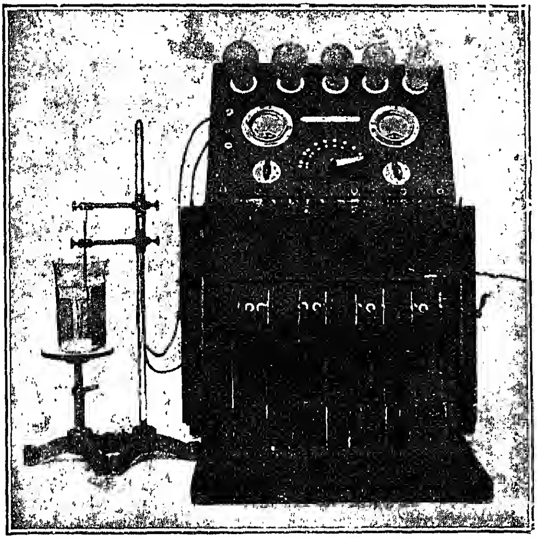


FIG. 16

ysis, since they usually yield a feeble current and must theresize. For analysis with stationary electrodes, a battery of 4 elements of 30–50 ampere-hour capacity is sufficient, whilst rotating electrodes may require 12 accumulators of this capacity. The various elements should connect with either a mercury or plug commutator, so that they may be grouped readily in parallel or in series or in mixed formation according to circumstances.

The *electricity supply current* may also be used and, if continuous, requires only the insertion of suitable resistances. If alternating, it must be converted into continuous current by an electrolytic rectifier, which serves particularly well when only low current intensities are required (1–1·5 amp.).

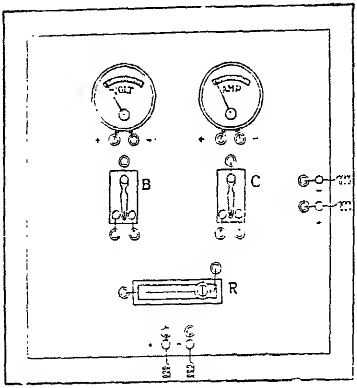


FIG. 17

Fig. 16 shows an electrolytic rectifier in connection with a small switchboard and the other arrangements necessary for electrolytic analysis.

**2. Distribution of the Current**—The switchboard for distributing the current is very simple. It includes essentially a rheostat (Fig. 17, *R*) to regulate the current, an accurate amperemeter and voltmeter, a commutator *C* for inserting or cutting-out the amperemeter in the circuit including the electrolytic cell, and an interruptor *B* to insert at will the voltmeter and measure the pressure at the terminals. In any laboratory the current may be distributed in the form most convenient to the particular circumstances.

**3. Electrodes and Supports.**—In general the electrodes are of platinum or iridised platinum and that on which the metal is deposited, that is, the cathode, is of greater surface than the anode.

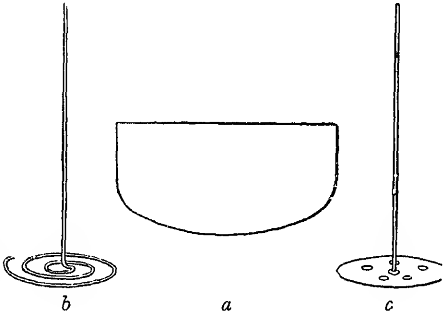


FIG. 18.

(*a*) WITH STATIONARY ELECTRODES. *Electrodes.* Of the numerous electrodes of different form and dimensions which have been suggested, those most suitable in practice are:

cases, especially when copper and
eing determined simultaneously, the
al may be replaced with advantage
cylinder of iridised, matte platinum
cm. in diameter and 5 cm. high (Fig.
his as much as 0·3 gram of lead may
ently deposited as peroxide, whilst
is deposited on the cathode.

. The most convenient and the
on are those of Classen. They con-
vy iron foot carrying a thick vertical
To the insulating rod are fixed by
ressure screws, the electrode holders,
assen electrodes being a ring furnished with three platinum
hich the dish rests and a binding screw for suspending the
those for Winkler electrodes two connecting screws (*see* Fig.
16).

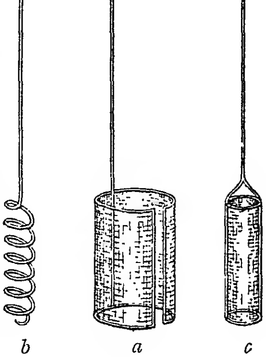


FIG. 19

(*b*) WITH ROTATING ELECTRODES. *Electrodes.* These may be: the Classen dish, within which the disc acting as anode revolves; or the Winkler cathode, inside which rotates a platinum spiral wound round a glass rod to give it solidity (Fig. 21). Other electrodes which are much in use and very convenient are those of Fischer, consisting of two concentric gauze cylinders (Fig. 20, *a*, *b*), insulated by quartz rods; the electrodes remain stationary, the liquid being kept in motion by a glass stirrer (Fig. 20, *c*) revolving inside the smaller cylinder.

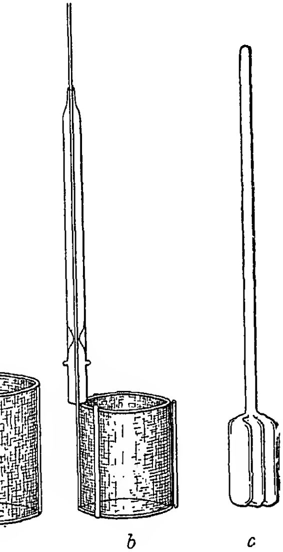


FIG. 20

*Stands.* These, besides supporting the electrodes, should permit of the
one of the electrodes or of a stirrer. In its simplest form, a
otating electrodes is shown in Fig. 21. One of the screws of
s replaced by a support carrying a rotating axis on which the

---

"Analysis of Bronzes for Ornamentation, so-called Nickel Bronzes" (*Ras-
ria*, 1909, XXXI, p. 50).

anode is fixed. The rotation may be imparted by a water turbine or an electric motor of adjustable speed. Much more perfect is the Fischer stand made for his electrodes and suitable also for use with the Classen dish (Fig. 22).

Another means for obtaining the rotation of the electrolyte is that proposed by Frary and based on the principle that any conductor carrying a current and situate in a magnetic field tends to move with a velocity depending on the intensities of the current and of the magnetic field. The arrangement of the apparatus is shown in Fig. 23. In practice, preference is given to mechanical methods of agitation.

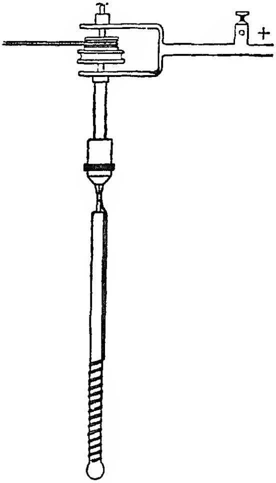


FIG. 21.

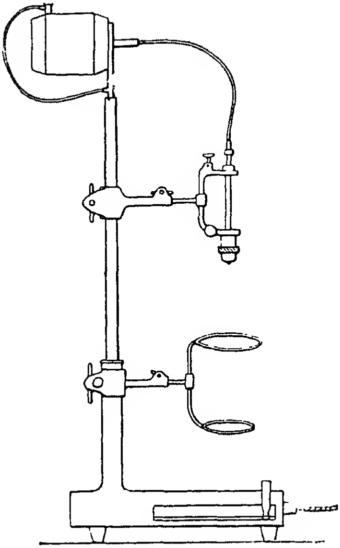
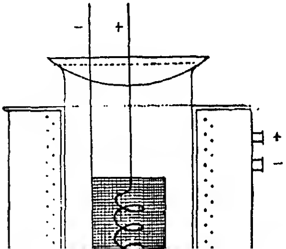


FIG. 22.



**Practical Rules.**—When use is made of Winkler's electrodes, which are the most practical, the electrolysis is carried out in a beaker which is fairly tall and not too narrow. The prescribed reagents are added, suitably diluted so that the electrodes remain completely immersed, and mixed. The beaker is placed to give the maximum resistance, the current started, neter and voltmeter inserted in the circuit, and the rheostat egulated until the measuring instruments indicate the proper voltage ; the instruments are then cut out.

e Classen capsule the same directions are to be followed. The ing the electrolyte is placed on the proper stand, the anode ntrally and a few centimetres from the bottom, the cover fitted as above.

otating electrodes are used, the procedure is the same : when s are in place, the rotating apparatus is started so as to give d velocity (number of turns per minute), the cover fitted, the ılated and the electrolysis continued.

**on of the End of the Deposition.**—When the prescribed time the deposition of the metal to be determined should be com- scertain if this is so, two means are used : (1) If the deposited ferent in colour from platinum (e.g., copper), the level of the s raised a few millimetres by addition of water ; if, after some inutes), the newly immersed part of the electrode shows no he metal being determined, the deposition is complete. (2) A electrolyte is removed and tested for the metal by its most actions.

**g of the Electrodes.**—With Winkler electrodes, the washing ple. The covers and thermometer are removed and washed the beaker grasped in the left hand and the supporting stand thout interrupting the current. The beaker is then rapidly y lowered and replaced by a small beaker, which contains, circumstances, distilled water or water acidified with sulphuric supported on the stand. After 10–15 minutes the cathode is ashed by a gentle jet of distilled water, then with alcohol and ether, dried in an oven at 60–70°, cooled in a desiccator and

e Classen dish two cases present themselves. If the electrolyte rgetic solvent action on the deposited metal, the covers are e anode detached and placed in a beaker which is kept near, ng emptied into the same beaker and washed with a little water. g is then completed with water, alcohol and ether, and the dish –70°, cooled in a desiccator and weighed. If, however, the s acid, it may attack the metallic deposit during these manipu- this case, the washing should be carried out without interrupting A small stream of distilled water is passed into the dish by Marriotte's bottle or otherwise, while at the same time the liquid usual washing and drying of the cathode effected.

**Dissolution of the Metallic Deposits.**—Deposits of copper, zinc, nickel, silver, etc., are dissolved in nitric acid ; tin and iron in hydrochloric acid ; antimony in nitric acid containing a little tartaric acid in solution ; lead peroxide in nitric acid with a little oxalic acid dissolved in it ; manganous-manganic oxide in dilute sulphuric acid containing hydrogen peroxide. When Winkler electrodes are used, it is very convenient to immerse them in a tall, narrow vessel fitted with a ground stopper and containing the proper acid, which may be used repeatedly.

## COPPER AND ITS ALLOYS

The more important commercial products are : refined and electrolytic copper and its various alloys with phosphorus, silicon, manganese, zinc, tin and nickel.

After the usual tests for industrial copper, methods for the analysis of its principal alloys will be given, beginning with alloys of copper with phosphorus, silicon and manganese, and coming later to the most important ones, namely, the ordinary and special brasses and the ordinary and special bronzes.

Alloys of copper with nickel and zinc (argentan) will be treated along with nickel and its alloys, and its alloys with tin and antimony (anti-friction metals) along with tin and its alloys.

### COPPER

The complete analysis of commercial copper, that is, the determination of the copper and of all the extraneous elements accompanying it in large or small proportions (Bi, Pb, Sb, As, Sn, Ag, Au, Fe, Ni, Co, Zn, S, Se, Te, C, P, Si, O, etc.) is a very long and delicate operation.[1] Beyond a determination of the copper, commercial analyses as a rule require only estimations of the more injurious elements, especially of bismuth, arsenic, phosphorus, antimony, lead, sulphur, nickel, iron and oxygen. Rapid and exact methods for determining these elements will, therefore, be given.

**1. Determination of the Copper** (by *electrolysis*).—5 grams of the metal in fine turnings, freed from fat by means of ether and from traces of iron from the sampling tool by means of a magnet, are placed in a tall, narrow beaker covered with a clock-glass or with an inverted funnel of rather less diameter than the mouth of the beaker. The metal is there covered with water and treated with 5–7 c.c. of conc. sulphuric acid, and p., using Winkler electrodes ; duration, 12–15 hours.

e deposition is complete (*see* p. 213), the electrolytic beaker without interrupting the current, by another small beaker ater faintly acidified with sulphuric acid, the cathode being er some time and washed first with water, then with alcohol, ith ether ; it is then dried at 70° and weighed. The increased sents copper and any silver present ; the latter metal is deter- 9 (below).[1]

pper deposited is not of a good, brilliant colour, but appears d spotted (presence of arsenic or bismuth), it is redissolved in 5–7 c.c. of conc. sulphuric acid and 15–20 c.c. of nitric acid uted to 250–300 c.c. and again electrolysed with addition of a ed lead sulphate (0·4 gram) and ferric sulphate (0·5 gram) races of arsenic and bismuth from being deposited with the

ual liquid free from copper, together with the wash water, e determination of antimony (*see* 5).

**mination of the Bismuth.**[2]—(*a*) ELECTROLYTICALLY. 10 sample are dissolved in 50 c.c. of nitric acid (D 1·33), 10 c.c. acid being added when the action is complete and the solution o dryness. The residue is taken up in 200 c.c. of water con- of sulphuric acid, the liquid being heated to boiling and the treated with 10 c.c. of phosphoric acid (D 1·71). When cold ith 30 c.c. of alcohol and, after 12 hours, filtered by decanta- recipitate, which contains all the lead and bismuth of the ashed first with a solution containing by volume about 1% cid, 5% of phosphoric acid and 15% of alcohol, and then with ion of ammonium sulphide and potassium cyanide [3] to remove es of copper, arsenic, antimony, etc. The precipitate is then the hot in nitric acid diluted with an equal volume of water, ered by decantation and the residue treated with aqua regia an equal volume of water, filtered and washed with boiling solution is evaporated with 12 c.c. of sulphuric acid until e fumes of sulphuric acid appear and, when cold, is treated

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ce of large quantities of silver, the electrolysis should be started at 30° of 0·1 amp. to deposit all the silver first. After some hours the current ed to 0·5–1 amp. and the electrolysis continued at the ordinary tem- all the copper is deposited.

of bismuth in copper (Abel and Field).—About 6 grams of the sample are ic acid, treated with about 0·3 gram of lead nitrate dissolved in a little monia until the reaction is alkaline and with a little ammonium carbonate. a little while, the liquid is filtered the precipitate washed with ammonia-filtered, the filter washed with water acidified with sulphuric acid and containing alcohol (in all 35 c.c. of alcohol should be used) and the liquid, about 300 c.c. in volume, electrolysed to determine the bismuth.[1] $ND_{100}$, i.e., current per 100 sq. cm. of electrode surface, = 0·1 amp.; duration = about 48 hours; maximum quantity of bismuth which can be deposited = 0·1 gram.

(*b*) GRAVIMETRICALLY.[2] 10 grams of the sample are dissolved in 60 c.c. of nitric acid (D 1·3) and the excess of acid expelled by evaporation on a water-bath. The residue is dissolved in 400 c.c. of water and neutralised, with continual shaking, by means of a very dilute solution of sodium hydroxide. As the acidity diminishes, more and more dilute alkali should be used in order to prevent separation of large clots of copper hydroxide. A slight excess of the alkali is added so as to produce a faint permanent turbidity, the liquid being made up to a litre and heated for an hour on the water-bath, a few drops of the alkali solution being added should the turbidity tend to disappear. A little further sodium hydroxide solution is then added to form a just perceptible precipitate and, after 15–20 hours, the precipitate—containing, besides copper, all the bismuth, iron, etc., of the sample—is collected on a filter, washed with cold water and dissolved in hot dilute hydrochloric acid. The bismuth is precipitated by rendering alkaline with ammonia, the excess of which is expelled on the water-bath (the copper should not precipitate), and the precipitate filtered off and washed with hot water. The precipitated bismuth hydroxide is redissolved in hydrochloric acid, the liquid diluted and precipitated with hydrogen sulphide, the precipitate filtered off and washed with yellow ammonium sulphide to dissolve any traces of antimony present and then with water. The bismuth sulphide is then dissolved in nitric acid and reprecipitated with ammonia, the precipitate filtered off, washed, dissolved in nitric acid and the solution evaporated in a tared porcelain crucible, the bismuth oxide being gently heated and weighed: $Bi_2O_3 \times 0{\cdot}8965 = Bi$.

**3. Determination of the Arsenic.**—5 grams of the sample[3] in fine borings are introduced into the flask used for arsenic distillation (*see* Iron, 6) and are gently shaken while 100–125 c.c. of conc. hydrochloric acid containing in solution 50 grams of ferric chloride free from arsenic[4] are added through a long-stemmed funnel. The flask is closed with the stopper carrying the pressure-regulating apparatus, connected with the pipette dipping into the ammonia solution, and heated gently to dissolve the metal completely; the flame is then increased and distillation carried on until the ammoniacal solution becomes faintly acid. At this point the distillation is suspended, the pipette removed and washed, and the arsenic determined iodometricall as indicated o p. 170.

n nitric acid, the excess of the latter expelled, and the liquid
1 c.c. of ferric chloride solution free from phosphorus and
line with ammonia. The precipitate is filtered off, washed
in hydrochloric acid, and the acid solution treated as described
if in presence of arsenic, on p. 176.

**nination of the Antimony** (Classen).—The solution from
pper has been removed electrolytically as in 1, together with
vater from the small beaker, is evaporated until the nitric
tely expelled; if the anode is brown, it is kept immersed for
few drops of hydrogen peroxide being added to dissolve the
osited on it.[1] The solution is diluted with water and sub-
action of hydrogen sulphide in the cold to prevent the pre-
he arsenic. The precipitate is filtered off and washed, and
oxide and sulphide and any tin oxide and sulphide dissolved
odium sulphide solution (D 1·225), 4–5 grams of potassium
added to the solution and the latter electrolysed in the Classen
= 0·15 amp.; duration = 10–15 hours.

**nination of the Lead** (by *electrolysis*).—5 grams of the
ated with 20–30 c.c. of nitric acid (D 1·18), the nitrous fumes
iling and the liquid diluted to 250–300 c.c. and electrolysed,
r cathode and a tared gauze cylinder anode, as described on
$_0$ = 0·5–1 amp., duration = 10–15 hours.
per is deposited on the cathode, lead is deposited as peroxide
At the end of the electrolysis, the electrodes are removed
vith water, and the anode, after further washing with dis-
ried at 180–200°, cooled and weighed: $PbO_2 \times 0{\cdot}866 = Pb$.
iese and considerable quantities of bismuth and iron are
amounts of the oxides of these metals are deposited on the
ie lead peroxide. In such case the deposit is dissolved in
ntaining a little alcohol, the solution being evaporated with
until copious white fumes appear, the residue being taken
a little alcohol added, and the lead sulphate separated and
other method consists in employing, for the determination
he lead sulphate which separates during the necessary pro-
electrolytic determination of the bismuth (*see* 2, *a*).

**nination of the Sulphur.**—The solution freed from copper
ectrolysis (*see* 6) is evaporated to dryness (to fix the sulphuric
sable to add a little sodium carbonate). The residue is taken
ydrochloric acid, the liquid being evaporated to dryness each
the whole of the nitric acid. The final residue is then dis-
of conc. hydrochloric acid and 50 c.c. of hot water and barium

the evaporating liquid, the peroxides deposited on it being caused solve by addition of a few drops of hydrogen peroxide. When residue is dissolved in water and the solution treated in the hot with gen sulphide to precipitate the arsenic, lead, antimony, etc. The pr is filtered off and washed, and the filtrate boiled to expel the h sulphide, treated with 1–2 c.c. of hydrogen peroxide, boiled and alkaline with ammonia to precipitate the iron. When considerab tities of iron are present, it is advisable to repeat this precipitati solution of the precipitate in a little hot, dilute sulphuric acid. T hydroxide separated is washed, dried and ignited ; it may be directly or dissolved in a little dilute sulphuric acid and estimated lytically (*see* p. 200).

The filtrate, or the mixed filtrates from the two precipitations, for the electrolytic determination of the nickel and zinc. First, 3 of ammonia and a few crystals of hydroxylamine sulphate are ad the nickel then deposited, the zinc being determined in the residual (*see* Analysis of Argentan).

When determination of the zinc is not required, the nickel may cipitated directly in the iron-free alkaline solution by alcoholic di glyoxime solution (*see* Gravimetric Analysis of Argentan).

**9. Determination of the Silver.**—2·5 grams of the sample solved in 100 c.c. of nitric acid diluted with an equal volume of wa solution being boiled to expel nitrous vapours and, without filtering to 95° and treated with a few drops of hydrochloric acid to precipi silver. The liquid is heated on the water-bath to separate the pre which is filtered off and washed with hot water, the silver being det in this impure silver chloride either electrolytically or gravimetric

(*a*) ELECTROLYTIC METHOD. The precipitate is dissolved in in 120 c.c. of 10% potassium cyanide solution, then diluted to and electrolysed with a current of 0·1 ampere.

(*b*) GRAVIMETRIC METHOD. The silver chloride is dissolved in a by digestion in the hot for some time, the solution being filtered and with nitric acid to reprecipitate the silver chloride, which is wei usual.

**10. Determination of the Total Oxygen.**—The oxygen pr commercial copper occurs largely as cuprous oxide and partly in c tion with extraneous metals. It is determined by causing it to with hydrogen at a high temperature and estimating the water A condition essential to accuracy is that the hydrogen must be dry and free from oxygen.

containing platinised asbestos heated to redness, the water absorbed by means of a U-tube charged with phosphoric

e determination, a blank test is made, the hydrogen being the glass or porcelain tube to be used in the determination on a combustion furnace; after about 10 minutes, a tared ydride tube, full of hydrogen and connected with a calcium to keep atmospheric moisture away, is attached, the tube ted to redness and the stream of hydrogen continued for . At the end of this time the burners are extinguished and ed to cool in the current of hydrogen; the U-tube should reciable increase in weight.

ermination, 10 grams of the sample, freed from grease and iron (*see* 1) are weighed in a perfectly dry porcelain boat, l in the *cold*, *dry* combustion tube, the air being then expelled drogen for 10–15 minutes. The phosphoric anhydride tube chloride tube are then attached and the tube heated strongly for 20–30 minutes.

eduction is complete, the tube is allowed to cool in the current nd the phosphoric anhydride tube weighed; the increased nts water, and this should correspond with the oxygen lost l in the boat.

nation of oxygen in copper is a very delicate and perhaps not eration. Metallographic examination gives information in this

⁂

od quality should be bright red and very ductile and malleable; uld be finely granular, of uniform colour and free from spots; ty should lie between 8·65 and 8·93, and it should contain more (electrolytic copper may contain 99·8–99·9% or even more). diminishes, the specific gravity, malleability and ductility

impurities, those of special influence on the mechanical pro- uth, lead, antimony, sulphur, arsenic, phosphorus, nickel, iron

Hampe, the presence of 0·02% Bi is sufficient to render copper t, while 0·05% makes it brittle also in the cold. Keller states taining a few thousandths of bismuth is unsuitable for electrical similar effect is exerted by lead in the proportion of 0·3–0·4%. once regarded as highly injurious, but less than 0·5% appears whatever proportion, it lowers the electrical conductivity, and g antimony is unfit for making brass. Sulphur, which may be ous ulphide, renders it c l short if present in greater quantity

## TABLE XXI

## Compositions of Commercial Copper

| ce. | Cu | Bi | As | Sb | Pb | Fe | Ni + Co | Ag | |
|---|---|---|---|---|---|---|---|---|---|
| (6 samples) . | 99·74–99·96 | 0·0–0·1 | 0·009–0·037 | 0·0–0·088 | 0–trace | trace–0·008 | 0·0–0·012 | 0·027–0·112 | |
| mples) . . | 99·19–99·51 | — | 0·025–0·061 | — | 0·006–0·206 | trace–0·037 | 0·279–0·467 | 0·014–0·028 | |
| ) . . . . | 99·325 | 0·052 | 0·130 | 0·095 | 0·061 | 0·063 | 0·076 | 0·072 | 0· |
| s) . . . | 97·66–99·91 | trace–0·53 | 0·009–0·094 | 0·00–0·102 | 0·0–0·042 | trace–1·248 | 0·005–0·413 | 0·009–0·084 | |
| es) . . . | 98·22–99·80 | 0·0–0·003 | 0·009–0·077 | trace–0·088 | 0·0–0·05 | 0·006–0·038 | 0·02–0·08 | 0·014–0·113 | |
| *coppers* | | | | | | | | | |
| r) . . . | 99·947 | 0·004 | 0·008 | 0·026 | — | 0·006 | 0·009 | — | |
| ishi) . . | 99·983 | trace | — | 0·012 | — | trace | — | — | |
| o-Montana) | 99·835 | — | — | 0·010 | trace | 0·004 | 0·007 | — | |
| r) . . . . | 99·989[1] | — | 0·00022 | 0·00065 | — | — | — | 0·00005 | |
| r) . . . . | 99·910[1] | 0·0017 | 0·01040 | 0·02730 | trace | — | — | 0·00004 | |

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[1] By difference.

opper is usually employed as a deoxidiser and for the prepara-ıor bronzes. It occurs mostly in cakes of metallic appear-e or steel-grey colour and sometimes with bluish reflections ; d has a crystalline structure.

s comprises essentially determinations of the phosphorus The impurities, derived from those of the copper used in its ay be estimated by the methods given on p. 214 for the nmercial copper.

**ination of the Phosphorus.**—0·5 gram of the finely pow-e treated in a covered dish with 10 c.c. of nitric acid (D 1·4), ing applied when the action slackens. If any unattacked after about 30 minutes, a few drops of hydrochloric acid y added and the liquid heated until solution is complete orated to dryness with 10 c.c. of nitric acid. The residue th hot water acidified with nitric acid and the liquid filtered d determine, if necessary) any traces of silica present, the ıade up to 250 c.c.

this solution are evaporated to 10 c.c. and treated with ıonium molybdate solution, the remaining procedure being mination of phosphorus in iron (*q.v.*).

**ination of the Copper.**—1 gram of the sample is treated itric acid (D 1·2) and 5 c.c. of hydrochloric acid in a covered olution is evaporated with 2–3 c.c. of sulphuric acid until hydrochloric acids are completely expelled and then heated ı until white fumes of sulphuric acid appear. When cool ıken up in hot water, the solution being mixed with 5–6 c.c. ) 1·4), made up to 200–250 c.c. and electrolysed (*see* p. 214) : ɔdes ; $ND_{100}$ = 0·3–0·4 amp. ; duration = 10–15 hours.

ɔper usually contains 9–15% P (sometimes, however, only 0·5–:e is given in practice to products with 10% P.

## CUPRO-SILICON

ɔn or copper silicide, also improperly termed silicon bronze, he electric furnace by reducing silica with carbon in presence is used especially for the deoxidation of brasses and bronzes paration of copper-silicon alloys containing small quantities sed in electro-technics for telephone wires, cables, etc. (alloys Si).

ises essentially determinations of the silicon and

**1. Determination of the Silicon.**—1 gram of the finely p
sample is treated with 10–20 c.c. of nitric acid (D 1·4) and heat
long time. After addition of 1–2 c.c. of hydrochloric acid, it is agai
for a short time and finally evaporated in presence of 2 c.c. of s
acid. The heating is continued on a sand-bath until copious whi
of sulphuric acid are emitted, the cooled residue being treated
water, filtered, and the filter thoroughly washed with hot water
with sulphuric acid. The filter, still somewhat moist, is place
upwards in a platinum crucible and the latter covered and heated
gently and later to ignition, the subsequent procedure being that
in estimating silicon in iron or steel (*see* p. 171).

**2. Determination of the Copper.**—The filtrate from the
acidified with 5–6 c.c. of nitric acid, made up to 250–300 c.c. and ele
to determine the copper. Winkler electrodes ; $ND_{100} = 0{\cdot}3$–0·
duration, 10–15 hours.

The commoner commercial types of cupro-silicon contain 10, 15, 20
of silicon.

## CUPRO-MANGANESE

The copper-manganese alloys are used as deoxidisers of cop
for the preparation of copper-manganese alloys with a low content
ganese—so-called manganese bronzes—and of the manganese bra
true manganese bronzes. Analysis includes determination of th
and manganese and, sometimes, of the impurities, particularly th
lead, iron and nickel.

**1. Determination of the Copper.**—1 gram of the sample is
in a covered dish with 10–15 c.c. of nitric acid (D 1·2), 6 c.c. of di
phuric acid (1 vol. acid to 1 vol. water) being added when the
complete and the liquid evaporated on a water-bath to eliminate t
acid and then heated on a sand-bath until copious white fumes of s
acid appear. When cool, the residue is stirred and gently hea
30 c.c. of water to dissolve the copper and manganese sulphates,
95% alcohol being added and the mixture left for one or two hou
insoluble residue, consisting usually of silica and lead sulphate, i
off and washed with a mixture of 60 c.c. of water, 10 c.c. of alcoho
c.c. of sulphuric acid, the filtrate being evaporated almost to dr
expel all the alcohol, and the residue taken up in water, diluted to
heated to 60–70° and electrolysed to determine the copper : Win
trodes ; temperature = 60–70° ; $ND_{100} = 0{\cdot}2$–0·3 amp. ; du

5 drops of hydrogen anode being kept immersed to dissolve the coating of man- e. The liquid is boiled for a few moments, the electrode d washed with water and the solution, when cold, made up a 300 c.c. flask. In aliquot parts the iron and manganese d either volumetrically or electrolytically.

ETRIC METHOD. In 50 or 100 c.c. the iron is determined by permanganate after reduction with amalgamated zinc.[1] In t part (50 or 100 c.c. according to the amount of manganese manganese is titrated by Volhard's volumetric method (*see* ese).

OLYTIC METHOD. In 100–200 c.c., according to the amount present, the iron and manganese are estimated as described ganese.

**ination of the Nickel.**—In an aliquot part of the 300 c.c. *e* 2), the nickel is determined by means of dimethylglyoxime the necessary quantity of tartaric acid (*see* Nickel Steel).

**ination of the Silicon and Lead.**—The residue remaining hen the copper and manganese sulphates are taken up in contains all the silicon and lead of the sample as silica and The latter is now dissolved in nitric acid containing ammo- nd the lead in the solution determined electrolytically in pper nitrate (*see* Lead-tin Alloys).

insoluble in nitric acid and ammonium nitrate consists of impure) and is filtered off, washed, ignited in a platinum ned, treated with hydrofluoric acid and again weighed; the represents silica (*see* Determination of Silicon in Iron).

er-manganese alloys containing little manganese (manganese dvisable to determine the copper separately in two distinct por- each) of the sample. When the copper is eliminated, the two ganese dioxide on the anodes are dissolved and made up together

⁂

ganese alloys contain about 25–30% of manganese with small on, silicon, etc. Two principal types are met with commercially: npure alloy with 72–74% Cu, 23–24% Mn, 2·5–4·5% Fe and 0·2– e pure alloy with 70–72% Cu, 28–30% Mn, 0·1–0·3% Fe and 0·05–

ith a low manganese content or *manganese bronzes*, used, owing the hot, for valves, tie-rods for locomotives, etc., contain on the Mn and such im urities as are usually met with in commercial

Ordinary brasses are alloys of copper and zinc in various prop always containing as impurities small quantities of lead, iron, tin an times nickel, arsenic, sulphur, phosphorus and bismuth. Their comprises the determination, by electrolytic or gravimetric meth the constituent elements and impurities.

## *A.* Electrolytic Methods

In a covered beaker, tall and narrow, 1 gram of the alloy in tur filings is dissolved at a gentle heat in 15 c.c. of nitric acid (D 1·2).

**1. Determination of the Tin.**—The solution is diluted with 30 of water and if it appears turbid owing to the presence of metastann it is evaporated to dryness, taken up in a few drops of nitric acid little water, heated for some time and filtered, the insoluble residu collected on a small, tight filter and the filtrate in a 350 c.c. elec beaker. The filter is washed, first with water faintly acidified wit acid and then with water alone, dried, ignited in a porcelain cruci weighed[1]: $SnO_2 \times 0{\cdot}7881 = Sn$.

**2. Determination of the Copper and Lead.**—The liquid free the metastannic acid is treated with 15 c.c. of nitric acid of D 1·2 (in of tin, it is not necessary to add fresh acid, since the evaporation solution to dryness is omitted), made up to about 200 c.c., allowed and electrolysed to determine simultaneously the copper and the Winkler cathode and matte gauze cylinder anode; $ND_{100} = 0{\cdot}3$ voltage, 1·8–2; duration, 10–15 hours. After half an hour or a when the greater part of the lead has been deposited as peroxide anode, 20 c.c. of 10% sulphuric acid are added to the electrolyte, carefully stirred by means of a glass rod.

When the deposition of the copper and lead is complete, the elec beaker is replaced, rapidly and without interruption of the curren small, tall and narrow beaker containing water acidified with su acid, this being replaced after some time by another beaker contain tilled water. Finally the electrodes are detached and washed, the with water, alcohol and ether, followed by drying at 70°, and th with water alone, followed by drying at 180–200°: $PbO_2 \times 0{\cdot}866$

**3. Determination of the Iron and Zinc.**—The liquid from the copper and lead have been separated and the wash water fr first beaker are evaporated together until white fumes of sulphu are emitted, in order to convert the zinc and iron nitrates into sul When cold it is taken up in water acidified with sulphuric acid, a fe lphates and the clear, hot solution treated with ammonia in After a short rest on the water-bath, the precipitated ferric tered off, washed, dried, ignited and weighed [1]: $Fe_2O_3$ ×

now contains only the zinc, which may be estimated with otating electrodes in the manner described below. In any if the brass contains more than 20% of zinc (shown by the er obtained), it is advisable to make up the volume of the ) c.c. and to determine the zinc on 150 c.c.[2]

*nation with stationary electrodes.* The ammoniacal solution :h lactic acid, then rendered faintly alkaline with sodium ated with 3 grams of ammonium oxalate and 5 grams of .e, heated gently to dissolve the salts and made up to about c. of lactic acid are then added and the still tepid liquid *:oppered* Winkler cathode [3]; Winkler spiral anode; $ND_{100}$ ).; voltage = 3–4; duration, 3–4 hours. After about 2 ·ent intensity is raised to 1 amp. and 2 c.c. of lactic acid electrolysis being continued until the deposition of the zinc

ı if all the zinc is deposited, a few drops of the electrolyte nd treated with a drop of potassium ferrocyanide: no turɔe produced, even after some time. Another method conting to the upper extremity of the stem of the cathode, by ıding screw, a stout copper wire previously cleansed by a ı in nitric acid, and bending this wire twice at right angles into the electrolyte for a few centimetres without touching if the wire does not show a faint bluish deposit of zinc after the deposition is complete. The electrolytic beaker is then small beaker filled with distilled water, the cathode being some time, washed with water, alcohol and ether and dried

*nation with rotating electrodes.* The ammoniacal solution is sulphuric acid, rendered alkaline with sodium hydroxide y acid by means of 25% formic acid solution; the liquid is o° and electrolysed: coppered Winkler cathode [3]; rotating rotations, 1000 per minute; temperature, 40–50°; $ND_{100}$

---

ıuch ferric hydroxide, it is advisable to precipitate twice to get rid of

**5. Determination of the Phosphorus.**—*See* Analysis of P Bronzes.

**6. Determination of the Arsenic, Sulphur and Bismuth** methods given for the analysis of copper (*q.v.*) are followed.

## *B.* Gravimetric Methods

In a small covered beaker, 0·5 gram of the sample is dissolved 15 c.c. of nitric acid (D 1·2) at a gentle heat.

**1. Determination of the Tin.**—When the action is comple solution is diluted with 15–20 c.c. of water and, if it appears turbi to the presence of metastannic acid, evaporated to dryness. The is heated for some time with a few drops of nitric acid and a littl and the metastannic acid filtered off, washed with hot water acidifi nitric acid, ignited and weighed: $SnO_2 \times 0{\cdot}7881 = Sn$.

**2. Determination of the Lead.**—The liquid freed from the meta acid, or the original solution if the alloy does not contain tin, is with 3–4 c.c. of concentrated sulphuric acid, evaporated to dryn heated on a sand-bath until white fumes of sulphuric acid appear. cool, the residue is taken up in 50 c.c. of water, gently heated and to dissolve the basic copper and zinc sulphates, allowed to cool and with 15 c.c. of 95% alcohol. After standing for 1–2 hours, the lead s separated is collected on a Gooch crucible, washed first with a mix 60 c.c. of water, 10 c.c. of alcohol and 0·5 c.c. of sulphuric acid ar with alcohol until the filtrate is neutral; the crucible is then drie air-oven in a roomy porcelain crucible: $PbSO_4 \times 0{\cdot}6831 = Pb$.

**3. Determination of the Copper.**—The filtrate from the lead s is evaporated until the alcohol is completely expelled, the residu heated to boiling with 100 c.c. of water and the copper precipitat hydrogen sulphide. The liquid is decanted on to a filter and the pre washed first with saturated hydrogen sulphide solution containing 20 c.c. of 2N-sulphuric acid in 100 c.c. and afterwards with sa hydrogen sulphide solution alone; the precipitate is dried and the determined as cuprous sulphide: $Cu_2S \times 0{\cdot}7986 = Cu$.

**4. Determination of the Iron.**—The filtrate is freed from hy sulphide, concentrated to a small volume, treated with a few d hydrogen peroxide to oxidise the iron, boiled and rendered alkali dilute ammonia. After a short rest on the water-bath, the preci ferric hydroxide is filtered, washed, ignited and weighed: $Fe_2O_3 \times$ $= Fe$. If the amount of ferric hydroxide is consi rabl th pr i f sulphur: $ZnS \times 0{\cdot}6709 = Zn$.

**nination of the Nickel.**—The filtrate from the zinc precipi- to expel hydrogen sulphide, concentrated, rendered faintly ammonia, and the nickel precipitated with alcoholic dimethyl- ıtion (*see* Analysis of Nickel Steel and of Argentan).

**nination of the Arsenic, Sulphur and Bismuth.**—The n for the analysis of copper (*q.v.*) are followed.

**nination of the Phosphorus.**—*See* Analysis of Phosphor

⁂

ıry brasses, besides copper and zinc, often contain small quan- and iron (sometimes up to 1%), in some cases tin (0·5–1%) and %) and, in general, the impurities present in the copper and zinc preparation.

ıss should exhibit a fracture of uniform colour and fine and homo- It should not contain more than 0·01% of antimony, as other- tle and unfit for hammering; it should not contain more than nuth or 0·1% of arsenic.

percentage compositions of some of the commoner commercial follows:

TABLE XXII

### Composition of Brasses

| Variety. | Cu | Zn |
|---|---|---|
| mbac, Mannheim gold (for cheap jewellery) | 85–95 | 5–15 |
| ts and plates . . . . . . . . . | 60–72 | 28–40 |
| es . . . . . . . . . . . . . . . | 65–70 | 30–35 |
| ting . . . . . . . . . . . . . . | 66–67 | 33–34 |
| . . . . . . . . . . . . . . | 60–67 | 33–40 |
| s (Fontainmoreau bronzes) . . . . . | 1–10 | 90–99[1] |
| elding . . . . . . . . . . . . . | 34–90 | 10–66[2] |

## SPECIAL BRASSES

ame are indicated those alloys of copper and zinc which con- uantities of one or more other elements (especially lead, tin, ese, aluminium) introduced for the purpose of imparting erties. The most important are as follows.

[1] Often contains 1–2% of lead.

[2] Sometimes contains also small quantities of tin.

Lead brasses are very soft and therefore suitable for casting worked at the lathe. Their analysis comprises, besides determina copper and zinc, also that of lead and of the impurities usually o in ordinary brass (iron, tin, nickel, sulphur, phosphorus, arsenic, b etc.). The analytical methods are exactly those used for ordinar (*q.v.*).

⁂

Lead brasses usually contain 1–3% of lead and such impurities as a in common brass.

## Tin Brasses

Tin brasses are used especially for making tubes, plates, valv for naval construction. They are analysed by the same methods as c brass (*q.v.*).

⁂

Tin brasses contain on the average 60–62% Cu, 37·5–39% Zn and Sn. In this category fall *Naval* brass, *Iton brass* and *Laveyssière bro*

## Manganese Brasses

Manganese is introduced in small quantities into brass to incr strength, elasticity and hardness. The constituents of these bra determined as with the complex brasses (*see* later).

⁂

The two types in most common use have the compositions : (1) 59– 40–41% Zn, traces of Mn, and (2) 58–59% Cu, 39–40% Zn, 1·8–2·2% M are used in marine construction, especially for making propellers.

The following table gives the compositions prescribed for manganes by the American Society for the Testing of Materials and by the Technica for Steam Plant of the United States Navy (*Industria*, 1914) :

TABLE XXIII

**Compositions of Manganese Brasses**

| | Cu | Zn | Sn (max.) | Fe (max.) | Al (max.) | Mn (max |
|---|---|---|---|---|---|---|

⁂

rasses in more common use have the following mean compositions :
*metal* : 55–60% Cu, 38–42% Zn, 1·5–2% Fe, 0–0·8% Sn.
*metal* : 58–60% Cu, 36–41% Zn, 0·7–1·8% Fe, 0–1% Sn.

## Aluminium Brasses

n brasses have properties similar to those of manganese and
nd find the same uses in naval construction. They are analysed
ods for complex brasses (*q.v.*).

⁂

nium brasses in more common use have the following mean per-
ositions (Guillet) :

) Copper, 68–70 ; zinc, 31–27 ; aluminium, 3–1.
) ,, 64–66 ; ,, 33–30 ; ,, 4–1.
) ,, 58–61 ; ,, 40·5–37·5 ; ,, 1·5–3.

## COMPLEX BRASSES

brasses have properties very similar to those of manganese
are largely used, particularly for making propellers, anchors,
o tubes, etc.

sses may contain at the same time : iron and manganese ;
minium ; iron, manganese, aluminium and, sometimes, tin.
s includes determinations of the components proper (Cu, Zn,
n) and of any extraneous elements present as impurities (Pb,
), and may be carried out electrolytically or by a combined
nd volumetric method.

### *A.* Electrolytic Method[1]

l covered beaker, 1 gram of the sample is dissolved in 10–12
acid (D 1·2) at a gentle heat.

**mination of the Tin.**—The solution is diluted with 15–20
and, if turbid owing to the presence of metastannic acid,
o dryness, the residue being taken up with a few drops of nitric
tle water. The liquid is heated for some time and the meta-
filtered off, washed with hot water acidified with nitric acid,
weighed : $SnO_2 \times 0·7881 = Sn$.

which separates is collected in a Gooch crucible and is washed fi a mixture of 60 c.c. water, 10 c.c. of alcohol and 0·5 c.c. of sulphu and then with alcohol until the reaction is neutral; it is then dried and weighed: $PbSO_4 \times 0{\cdot}6831 = Pb$.

**3. Determination of the Copper.**—The filtrate is evaporated to dryness to eliminate the alcohol, the residue being diluted with 150 c.c. and electrolysed at the ordinary temperature. Cathode, electrode; anode, spiral; $ND_{100} = 0{\cdot}1–0{\cdot}2$ amp.; voltage, 1·7–2 tion, 15–16 hours.

During the whole course of the electrolysis, the voltage at the te should never exceed 2, so that it is advisable to use a single accu or a battery of accumulators joined in parallel. At the completio deposition, the electrolytic beaker is lowered slowly and the el washed as they emerge. The washing of the cathode is complet water, alcohol and ether, and the weight determined after drying

**4. Separation of the Iron and Manganese.**—The spiral which is covered with a black coating of manganese dioxide, is in in the liquid from which the copper has been separated, this being with addition of 3–4 drops of hydrogen peroxide until the manganese is completely dissolved. The spiral is withdrawn and washed, solution concentrated to 30–40 c.c. and poured, little by little a shaking, into a solution of 10 grams of pure sodium hydroxide in 3 of water contained in a platinum or porcelain dish. The iron and t ganese are precipitated as oxides, while the zinc and aluminium p solution as sodium zincate and aluminate. The liquid is heated to diluted with boiling water and filtered, the filtrate being collected i litre beaker containing about 100 c.c. of 20% sulphuric acid and t washed with hot water. The oxides separated are dissolved in dilute sulphuric acid containing a few drops of hydrogen peroxide solution again poured into sodium hydroxide solution of the conce mentioned above, the latter being heated to boiling, diluted and and the filtrate collected in the same half-litre beaker as the ot

(*a*) DETERMINATION OF THE IRON. The ferric and manganese hy are redissolved in the least possible quantity of 10% sulphuric aci drops of hydrogen peroxide being added and the solution heate greater part of the free acid is neutralised with ammonia and the poured into a boiling solution of 6–7 grams of ammonium oxalate i water; after addition of 5–6 c.c. of 2% hydrazine sulphate solut dilution to about 200 c.c., the liquid is electrolysed to determine (*see* Ferro-manganese, Electrolytic Analysis).

e manganese determined as indicated in the electrolytic analysis ganese.

**mination of the Zinc.**—If not already acid, the solution ne zinc and aluminium is acidified with dilute sulphuric acid, f necessary to reduce the volume to 200–250 c.c., rendered n sodium hydroxide, acidified slightly with formic acid and with rotating electrodes to determine the zinc (*see* p. 225).

**mination of the Aluminium.**—The liquid from which the n removed, together with wash water, is treated with ammo- e and ammonia until the reaction is alkaline, boiled for some aluminium hydroxide filtered off, washed, dried, ignited and $_2O_3 \times 0{\cdot}5303 = Al$.

**mination of the Phosphorus, Sulphur, Bismuth, Arsenic,** inary Brass.

## ombined Gravimetric and Volumetric Method

of the sample are dissolved in 20 c.c. of nitric acid (D 1·2) at :.

**nination of the Tin, Lead and Copper.**—The liquid is 15--20 c.c. of water, and the tin, lead and copper determined ly as in ordinary brass (*q.v.*).

**nination of the Iron, Manganese, Zinc and Aluminium.** from which the copper has been separated as sulphide is reduce its volume to about 200 c.c. and to expel the hydrogen iron being oxidised by addition of a few drops of hydrogen the cooled liquid made up to 300 c.c.

IETRIC DETERMINATION OF THE IRON. The iron in 50 c.c. on is reduced with zinc amalgam and titrated with perman- usual way.

IETRIC DETERMINATION OF THE MANGANESE. Two other n of 50 c.c., are used for the determination of the manganese method (*see* Ferro-manganese), one for the preliminary test r for the actual determination.

MINATION OF THE ZINC. A further quantity of 50 c.c. is lline with ammonia and then neutralised with formic acid; c.c. of this solution 4 c.c. of 50% formic acid are added and pitated by hydrogen sulphide. The liquid is left overnight he precipitation and is then filtered through a filter-paper of ure and washed with a dilute solution of ammonium formate (*d*) DETERMINATION OF THE ALUMINIUM. The liquid from whi zinc has been removed is concentrated in a porcelain dish to small v the iron being then oxidised with hydrogen peroxide and the soluti dered alkaline with pure potassium hydroxide solution, boiled, with boiling water and filtered. The filter is washed with hot wa the filtrate acidified with nitric acid, rendered alkaline with ammon heated to boiling for a short time. The precipitated aluminium hy is filtered off, washed, dried to some extent, ignited in a platinum c and weighed: $Al_2O_3 \times 0{\cdot}5303 = Al$.

**3. Determination of the Phosphorus, Sulphur, Arsenic, Bis etc.**—*See* Ordinary Brasses.

⁂

Of these complex brasses the one most largely used is the so-called metal," of the following mean composition: 54–62% Cu, 38–40% Zn, Mn, 0·4–1·2% Fe, 0·02–2·5% Al, 0–0·5% Pb and 0–3% Sn.

## ORDINARY BRONZES

Analysis of ordinary bronzes includes, besides determinations constituent metals (copper, tin and sometimes zinc), also those extraneous metals often present in small quantities (lead, iron, an nickel, manganese, phosphorus, arsenic, sulphur, etc.). Electrol gravimetric methods may be used.

### *A.* Electrolytic Method

In a covered beaker, 1–3 grams of the alloy, as filings or turni treated in the cold with 15–20 c.c. of nitric acid (D = 1·3), the liqu heated gently when the action slackens and finally evaporated al dryness.

**1. Determination of the Tin.**—The residue is taken up wit drops of nitric acid, 50 c.c. of water being mixed in and after about on the water-bath, the liquid filtered through a compact filter-pa the residue on the filter washed with hot water acidified with ni (1 of acid to 100 of water). The filtrate is utilised as described in 3 The metastannic acid separated may be dried, ignited and weighe may contain various impurities (especially copper and phosphor when an exact analysis is required the following procedure is adv

---

[1] The method of fusion with sulphur and sodium carbonate indicated for metric analysis of bronzes (*see* p. 234) may also be used and, when the anti

nd 10–15 c.c. of sodium sulphide solution (D 1·225) in a small water-bath until the metastannic acid is completely dissolved. n with 10–15 c.c. of water and addition of a little sodium sul- ed in a little water to reduce polysulphides, the liquid is again short time and filtered by decantation, the filtrate being collected conical flask. The residue is again treated with 10–15 c.c. of ide solution, heated, reduced with sulphite, diluted, filtered and h hot water containing a little sodium sulphide until about of filtrate are collected. The lead, copper, iron, etc., contained stannic acid remain on the filter as sulphides. The filter is en burnt in a small dish, the residue being dissolved in a little D 1·3) and the solution obtained added to the liquid in which lead, zinc, etc., are to be determined.

ds the determination of the tin and antimony, hydrochloric with an equal volume of water is added gradually and with der a draught hood) to the solution in sodium sulphide until ows an acid reaction ; 25–30 c.c. of concentrated hydrochloric n added and the liquid boiled to dissolve the separated sul- ng, if necessary, a few crystals of potassium chlorate.

old, the solution—which contains sulphur and is turbid—is aline with ammonia and then heated with 5 grams of oxalic all the tin hydroxide precipitated by the addition of ammonia d, 7 grams of ammonium oxalate are added, the liquid heated nd hydrogen sulphide passed for about 15 minutes through liquid. Under these conditions, any antimony present is alone .

ng allowed to cool somewhat in the current of hydrogen sulphide, filtered, the filtrate being collected in a ½-litre beaker and the cted with a hot 1% oxalic acid solution saturated with hydrogen The antimony sulphide precipitate remaining on the filter is cording to 2 (below).

ate is treated with 30 c.c. of conc. hydrochloric acid and 20 monium oxalate, boiled for a short time to eliminate hydrogen few drops of hydrogen peroxide added, heated again for a short d to cool to 40–50°, made up to about 300° and electrolysed, der a hood, to determine the tin : coppered Winkler cathode [1] ; e ; $ND_{100} = 1$ amp. ; voltage = 3–4 ; temperature, 40–50°, n (with 0·1–0·3 gram Sn) 4-5 hours.

e deposition of the tin is complete, the electrolytic beaker is ithout interrupting the current, by another full of water ; after cathode is detached, washed with an abundant supply of water

**2. Determination of the Antimony.**—The filter-paper wit antimony sulphide is heated in a beaker with 4 c.c. of 50% sodium hyd solution and 20–30 c.c. of sodium sulphide (D = 1·225) until the ant sulphide is completely dissolved. After some time the liquid is directly into the Classen dish, the vessel and filter being washed with c.c. of sodium sulphide. The filtrate is treated with 5–6 grams of pot cyanide to decolorise the sodium sulphide and to prevent format polysulphides during the electrolysis, which is carried out at the or temperature. Cathode, Classen capsule; anode, disc or spiral; = 0·15–0·18 amp.; voltage = 1–1·2; duration (0·1–0·15 gram 15–18 hours.

When the antimony is all deposited, the anode is withdrawn, th sule rapidly emptied, washed with water, alcohol and ether, and dr 70°.

The antimony is afterwards removed from the dish by treatmen nitric acid (D 1·2) containing a little tartaric acid in solution.

**3. Determination of the Copper, Lead, Iron and Zinc.**—The from which the metastannic acid was separated (*see* 1) is acidified 15–20 c.c. of nitric acid (D 1·2), mixed with the nitric acid solution oxides extracted from the metastannic acid and the whole treated as analysis of ordinary brass (*q.v.*).

**4. Determination of the Nickel.**—*See* Nickel Bronzes.

**5. Determination of the Manganese.**—*See* Manganese Bronz

**6. Determination of the Silver.**—5–10 grams of the samp treated with nitric acid and freed from metastannic acid in the or way. In the filtrate the silver is precipitated with hydrochloric a the procedure followed for the determination of silver in copper.[1]

**7. Determination of the Phosphorus.**—*See* Phosphor Bronze

**8. Determination of the Arsenic.**—*See* Copper.

**9. Determination of the Sulphur.**—2 grams of the sampl treated with nitric acid and the stannic acid separated as usual. the filtrate the copper is eliminated by electrolysis in nitric acid sol the residual liquid being evaporated to dryness and the sulphur then mined as in copper (*q.v.*).

## *B.* Gravimetric Method

**1. Determination of the Tin.**—In a covered beaker, 1–2 gra the alloy as filings are treated with 15–20 c.c. of nitric acid (D 1·3 sodium sulphite until it becomes pale yellow.[1] The liquid is and, the precipitate washed with water containing a little sodium l then with hydrogen sulphide solution; the filter is burnt in and the residue dissolved in a little nitric acid and the solution filtrate from the metastannic acid containing the bulk of the , zinc, etc., dealt with as in 3.

ion contains all the tin and antimony present as sulpho-salts. s treated in a ¾-litre conical flask with 6 grams of caustic potash, artaric acid and, slowly and, if necessary, with cooling, with % hydrogen peroxide to give complete decoloration, that is, he sulphide completely into sulphate. The liquid is boiled ne to expel excess of hydrogen peroxide, allowed to cool, neu fully with oxalic acid, treated with an excess of 3–5 grams of liluted to 250–300 c.c., heated to boiling, and a moderate current sulphide passed through the boiling liquid for about an hour. then allowed to cool somewhat and any precipitated antimony lected in a tared Gooch crucible, and washed first with 1% solution saturated with hydrogen sulphide and afterwards with hot acetic acid saturated with hydrogen sulphide.

mine the tin, the filtrate is rendered slightly alkaline with idified with acetic acid, and the tin precipitated with hydrogen fter the precipitation, the liquid is left at rest for about half the water-bath to facilitate the separation of the precipitate, iltered, being washed with hydrogen sulphide solution containmmonium sulphate in solution. The tin sulphide thus obtained 20°, converted by ignition into oxide and weighed.

**mination of the Antimony.**—The antimony sulphide in the le is converted by any of the known methods [2] into the tri- l weighed directly: $Sb_2S_3 \times 0{\cdot}7142 = Sb$.

**mination of the Lead, Copper, Iron, Zinc, etc.**—The ined after the action of nitric acid on the alloy, together with id solution of the metals extracted from the metastannic acid, ith 2–3 c.c. of conc. sulphuric acid, the further procedure being the analysis of ordinary brasses (*q.v.*).

**mination of the Manganese, Silver, Phosphorus, Arsenic ur.**—*See* preceding method.

⁂

ositions of bronzes vary widely with the requirements as regards asticity, colour, sonority, etc.

for machine gearing and the old, highly elastic, tenacious and

As a rule commercial bronzes, besides copper and tin, contain small tities of other elements (especially zinc, iron, manganese, nickel, lead, ant phosphorus, arsenic, sulphur, etc.), which, even in small proportions, ma foundly modify the properties of the alloy (*see* Special Bronzes) ; so much the case that it is not always easy to decide if these elements are impur the raw materials used or if they have been added to obtain certain properties.

Zinc in small quantities (0·5–2%) renders bronze more easy to ca increases its strength and elasticity ; if, however, the proportion is greater than 2%, the bronze loses its hardness and strength and assum perties approximating to those of the brasses.

The presence of lead is especially harmful in bronzes for machines and even if it is only slightly greater than 0·5%, since it diminishes the homo of the alloy. In proportions not exceeding 1·5%, iron exerts an action an to that of zinc and increases considerably the hardness of the bronze. antimony, bismuth and sulphur are highly injurious, and even in the pro of 0·1% render the bronze brittle. Nickel, manganese and phosphorus i the quality of the alloy and are often added (*see* Nickel-bronze, Man bronze, Phosphor-bronze, etc.).

## SPECIAL BRONZES

These are copper-tin alloys containing another element added definite object. Those in more common use are : phosphor-, manganese-, lead-, nickel-, lead-nickel- and aluminium-bronzes.

### Phosphor-bronzes

Phosphor-bronzes are so called because during their preparation quantity of phosphorus is added as phosphor-copper or phosphor-t a view to reduce the metallic oxides contained in the metal and, th to impart greater hardness, strength, elasticity, etc. The attempt is made to add the quantity of phosphorus just necessary for the deox (there may, therefore, be phosphor-bronzes free from phosphorus most only a slight excess, so that only a very small amount passes i alloy. The analysis includes determinations of the usual cons and impurities and also that of phosphorus.

**1. Determination of the Phosphorus.**—(*a*) In absence of A 2 grams of the sample are dissolved in aqua regia or in hydr acid and potassium chlorate, the solution being repeatedly evapor dryness with hydrochloric acid, the residue then dissolved in dilute chloric acid and water and the phosphoric acid precipitated with amr molybdate as in the determination of phosphorus in iron (*see* p. 17

(*b*) In presence of Arsenic. Aft the repeated e ap of Phosphorus in Iron in presence of Arsenic).

**mination of Tin, Copper, Zinc, etc.**—*See* Ordinary Bronzes.[1]

⁂

ronzes for bushes, pistons, etc., subject to attrition, quantities of arying from 0·25 to 2·5% are sometimes present with a view to ite special effects. In ordinary phosphor-bronzes smaller quannd (less than 0·25%).

## Silicon-bronzes

e used especially for telegraph and telephone wires, as they ectrical conductivity and resistance to tension. Their analysis

**mination of Silicon.**—2–10 grams of the sample, according osed silicon content, are treated with aqua regia (3 parts of acid and 1 part of nitric acid), the solution being evaporated e residue taken up twice with about 15 c.c. of concentrated acid and evaporated, and the residue heated in an oven at er the silica completely insoluble. The residue is treated with acid, the subsequent procedure being as in the determination ron. In the present case also the purity of the silica must be by treatment with sulphuric and hydrofluoric acids.

**mination of the Tin, Iron, Zinc, Nickel, Phosphorus, c.**—As with ordinary bronzes[2] (*q.v.*).

⁂

nzes, besides a little tin and often a little zinc, contain very small silicon (0·05–1%) introduced in the form of silicon-copper as a According to Hampe the best bronzes for telegraph and telephone e following percentage compositions :

TABLE XXIV

### Compositions of Silicon-bronzes

| | Cu | Sn | Si | Fe | Zn |
|---|---|---|---|---|---|
| lephone wires . | 97·12 | 1·14 | 0·05 | trace | 1·12 |
| legraph wires . | 99·94 | 0·03 | 0·03 | trace | — |

## Lead-bronzes

nzes, also called American bronzes owing to their widespread ca, besides copper and tin contain considerable quantities of solved in dilute hydrochloric acid and hot water (400–500 c.c.) and th solution treated with hydrogen sulphide. The precipitate is washe a Gooch crucible with hot water saturated with hydrogen sulphid acidified with hydrochloric acid and the filtrate evaporated to dryness nitric acid.

The residue is dissolved in a little nitric acid and the phosphori precipitated with ammonium molybdate as in the determination of phorus in iron.

⁂

The following table gives the compositions of various types of comm lead-bronzes (Guillet, Muspratt, Ledebur) :

TABLE XXV

### Composition of Lead-bronzes

| | Cu | Sn | Pb | Zn | P | Fe | Sb | Ni |
|---|---|---|---|---|---|---|---|---|
| 1 . . . . | 84·70 | 10·05 | 4·00 | 0·46 | 0·11 | — | 0·14 | — |
| 2 . . . . | 84·00 | 3·00 | 4·56 | 8·50 | — | — | — | — |
| 3 . . . . | 83·85 | 8·32 | 7·36 | 0·13 | 0·31 | trace | — | — |
| 4[1] . . . | 79·70 | 10·00 | 9·50 | — | 0·80 | — | — | — |
| 5 . . . . | 73·50 | 9·50 | 9·50 | 9·50 | — | 0·50 | — | — |
| 6 . . . . | 78·01 | 10·36 | 10·45 | — | 0·57 | 0·09 | — | 0·26 |

## Manganese-bronzes

Manganese-bronzes, which should not be confused with mang brasses—often improperly given this name—or manganese-copper are composed essentially of copper and tin with small proportions of ganese (1–3%). Their analysis comprises :

**1. Determination of the Tin.**—As in ordinary bronzes.

**2. Determination of the Lead, Copper, Iron, Manganese Zinc.**—The liquid from which the metastannic acid has been sepa together with the solution of the metals occluded in the metastannic is evaporated with sulphuric acid and the separate determinations c out as with complex brasses.

**3. Determination of the Phosphorus, Arsenic and Sulphur** Ordinary Bronzes.

---

[1] Type adopted by the Italian State Railways.

| | | | | |
|---|---|---|---|---|
| 92 | 8 | — | 1 | — |
| 84 | 14 | — | 2 | — |
| 82 | 15 | — | 3 | — |
| 92 | 8 | 3 | 0·5 | trace |

## Nickel-bronzes

tion of small proportions of nickel to bronzes increases the
l lustre and imparts a pleasing, golden colour.

lysis includes :

**mination of the Tin.**—2 grams of the sample are treated , tall, narrow beaker with 20 c.c. of nitric acid (D 1·2), the g evaporated to dryness, taken up with a few drops of nitric water and heated for a short time on the water-bath. The acid is collected on a close filter-paper and, being in small y be weighed directly after washing with hot water acidified cid, drying and calcining.

**mination of the Lead, Copper, Iron, Nickel and Zinc.**—
its are determined in the liquid freed from metastannic acid ods given for the analysis of argentan (*see* later).

**mination of the Phosphorus, Arsenic and Sulphur.**—*See* onzes.

⁂

nzes have the following mean composition : 88–89% Cu, 2–3% , 2–3% Ni, and 0·1–0·3% Pb.

## Lead-nickel-bronzes

very soft and are also called plastic bronzes and serve mostly n metals. Their analysis comprises :

**mination of the Tin.**—2 grams of the alloy are dissolved tall, narrow beaker with 20 c.c. of nitric acid (D 1·3), the solu- ted to dryness, and the analysis continued as with ordinary ).

**mination of the Lead.**—The solution freed from metastannic solution of the oxides of copper and lead retained by the meta- are evaporated together to a small volume and then heated given for the gravimetric analysis of ordinary brasses.

**3. Determination of the Copper, Iron, Nickel and Zin** ELECTROLYTICALLY. The liquid freed from lead is evaporated un alcohol is expelled and the residual liquid mixed with 20 c.c. of nitr and electrolysed as in the case of argentan.

(*b*) GRAVIMETRICALLY. The liquid freed from lead is evapora eliminate the alcohol, mixed with 200–250 c.c. of water, heated to and the copper precipitated with hydrogen sulphide, the subsequer cedure being that described for the gravimetric analysis of argenta

**4. Determination of the Phosphorus, Arsenic and Sulp** *See* Ordinary Bronzes.

⁂

Lead-nickel-bronzes have the following mean composition : 64% C Pb, 5% Sn, and 1% Ni.

## Aluminium-bronzes

Aluminium-bronzes have a fine, golden-yellow colour and are us making vases, ornamental articles, etc. They consist essentially of and aluminium (3–10%) and often contain small quantities of silic iron. Their analysis includes :

**1. Determination of the Silicon.**—1 gram of the alloy is gently with 10 c.c. of nitric acid (D 1·2) and the solution evaporate 10 c.c. of 50% sulphuric acid until white fumes of sulphuric acid a The residual liquid is mixed with 30 c.c. of water, heated for some tin when cold, filtered through a small filter ; the residue of more or les silica is washed, dried, calcined in a platinum crucible and weighed. then treated with hydrofluoric acid, etc., as in the determination of in iron.

**2. Determination of the Copper.**—The filtrate is treated wi c.c. of nitric acid, diluted to about 150 c.c. and subjected to elect (*see* Electrolytic Determination of Copper in Ordinary Brasses).

**3. Determination of the Iron and Aluminium.**—After r of the copper, the liquid is rendered alkaline with ammonia, boiled fo time and the precipitated aluminium and ferric hydroxides filter washed, calcined and weighed. The oxides are then fused with pot bisulphate, the residue taken up in dilute sulphuric acid and the the solution determined electrolytically or volumetrically. The ir aluminium are thus obtained separately.

|  |  |  |  |  |
|---|---|---|---|---|
| oiles) | 94·9 | 4·7 | 0·41 | 0·10 |
|  | 95·4 | 4·0 | 0·33 | 0·12 |
|  | 97·0 | 2·7 | 0·10 | 0·20 |

## ZINC AND ITS ALLOYS

ace zinc as such will be treated and methods described for ts common impurities ; technical tests for zinc dust are also egards the numerous alloys in which zinc occurs, those with alt with under copper and its alloys and those with nickel under s alloys.

## ZINC

neous elements commonly found in commercial zinc are lead, mium. Small quantities of arsenic, antimony and sulphur found and in remelted zinc also tin, but only rarely are traces icon, phosphorus, copper, nickel, cobalt, etc., found.

tial determinations to be made on commercial zinc are those and cadmium. It may sometimes be of interest to estimate ntimony and sulphur, but as a rule it is sufficient to test qualihe other elements.

**nination of the Lead, Iron and Cadmium** (according to romm [1]).—To 100 grams of the sample and 200 c.c. of water, ing about 2 litres, nitric acid is added gradually until, with g, the metal is completely attacked.

'on obtained is then treated with ammonia until the zinc irst separating redissolves, and then diluted to about two litres, nmonium sulphide being next added in small quantities and until the lead, iron and cadmium are completely precipitated hide begins to appear.[2] The liquid is kept at 80° for a short ate separation of the precipitate, which consists of lead, cadtc., sulphides mixed with zinc sulphide, and is filtered off when nt solution becomes clear. The precipitate is treated on the ot, dilute hydrochloric acid,[3] which dissolves lead, cadmium

---

*nalyt. Chem.*, 1897, p. 37.

ortion of the liquid, filtered and treated with ammonium sulphide, should ly white precipitate.

chloric acid (20 c.c. of conc. HCl made up to 100 c.c.). It is advisable l in a wash-bottle and to wash with it also the flask in which the precipice. About 150–200 c.c. to be used in all.

in brass (*see* p. 220).

(*b*) Determination of the Cadmium. The liquid freed fro sulphate is evaporated until the alcohol is expelled, neutralised with ammonia, treated for every 100 c.c. of liquid with 10 c.c. hydrochloric acid (D 1·125) and then with hydrogen sulphide. T cipitate is filtered off, washed with saturated hydrogen sulphide and dissolved in nitric acid (D 1·2), the solution being evaporat tared platinum crucible in presence of a slight excess of sulphur the excess of the latter being eliminated and the residue heated ger weighed: $CdSO_4 \times 0{\cdot}5392 = Cd$.

(*c*) Determination of the Iron. The excess of hydrogen s is eliminated from the filtrate from the cadmium sulphide, the iro oxidised by a few drops of hydrogen peroxide or bromine water, and a added until the reaction is alkaline. After a short rest on a wat the precipitated ferric hydroxide is filtered and washed. To free cipitate from all traces of zinc, it is redissolved in dilute hydrochlo again precipitated with ammonia, filtered off, washed with slightly niacal water, dried, ignited and weighed: $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

**2. Determination of the Sulphur, Antimony and Arsenic** ing to Gunther [1]).—100 grams of the sample are placed in a lar furnished with a delivery tube and with a tapped funnel, the which, bent up at the end, reaches almost to the bottom of the vess air is expelled by means of pure hydrogen washed by passing it silver nitrate solution and the delivery tube connected with two bottles, the first containing a solution of cadmium cyanide in po cyanide and the second silver nitrate solution, pure dilute sulphu being then gradually introduced by means of the tapped funnel u metal dissolves completely. When evolution of gas ceases, a n current of hydrogen is passed through the apparatus to displace the products of the reaction. The first washing bottle retains the sul cadmium sulphide, which is filtered off and converted into sulphat and weighed.

In the second bottle, if hydrogen arsenide and antimonide are metallic silver and silver antimonide [2] separate. The precipitate is off, washed and dissolved in nitric and tartaric acids, the silver be precipitated as chloride, which is filtered off, washed, dried and In the filtrate, the greater part of the acidity is neutralised with a

---

[1] *Zeitschr. analyt. Chem.*, 1881, XX, p. 503.

[2] The reaction occurs according to the equations:

$$SbH_3 + 3AgNO_3 + aq. = Ag_3Sb + 3HNO_3 + aq.$$
$$2AsH_3 + 12AgNO_3 + 3H_2O = 12Ag + 12HNO_3 + As_2O_3.$$

of oxide. The silver corresponding with the amount of anti-
l ($Ag_3Sb$) is deducted from the total silver found, and the arsenic ng with the remainder calculated: $2As = 12Ag$.

⁂

zinc of good quality should not contain more than 1·5% of ex- ments (Pb, Fe, Cd, Cu, etc.) and not more than 0·1% of As, Sb and The presence of lead in small quantities (0·2–1·5%) in zinc is not l, but with more than 2–3% of lead, zinc becomes brittle and diffi- into sheets. Iron rarely occurs in greater proportion than 0·2% amount is not injurious, but in greater quantity it renders the metal ittle. Cadmium also is always present in small proportion (0·01– s not deleterious unless the zinc is to be used for making zinc white. only in remelted zinc. Arsenic, antimony and sulphur are usually ces, but if together they exceed 0·1% the metal is very brittle; a t is exerted by copper to the extent of 0·5%. Carbon and silicon, sometimes be present in small proportions, have no appreciable ion.

positions of various refined zincs of commerce are as follows (Schnabel, Hollard):

TABLE XXVIII

**Composition of Zincs**

| | Zn[1] | Pb | Fe | Cd | Ag | Cu | Sb | As | S | Si | C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| . . | 98·782 | 1·118 | 0·024 | 0·012 | — | — | 0·022 | — | — | — | — |
| . . | 98·930 | 1·000 | 0·030 | 0·018 | — | — | — | — | — | — | — |
| rtha<br>. . | 99·981 | — | 0·019 | — | — | — | — | — | — | — | — |
| d'Art<br>M. | 98·904 | 1·070 | 0·016 | 0·010 | — | — | — | — | — | — | — |
| ra . | 99·757 | 0·192 | 0·049 | trace | — | 0·002 | — | — | — | — | — |
| . . | 98·752 | 1·1524 | 0·0073 | 0·0705 | 0·0002 | trace | 0·0020 | 0·0015 | 0·0035 | 0·0022 | 0·0075 |
| . . | 99·868 | 0·1094 | 0·0065 | 0·0075 | trace | 0·0005 | 0·0018 | 0·0005 | 0·0005 | 0·0035 | 0·0006 |

## ZINC DUST

cial zinc dust constitutes a mixture of very finely divided zinc zinc oxide and variable proportions of cadmium, iron, lead, bon, etc., and is used as a reducing agent. It is usual to deter- educing power towards solutions of potassium dichromate or ; in some cases, however, the volume of hydrogen obtained action of dilute hydrochloric acid is measured, the quantity of t and hence the commercial value being deduced therefrom.

**ermination of the Reducing Power.**—*Reagents*: N/2-potasis continued for 10–15 minutes—until all the zinc is dissolved. The is emptied and washed into a half-litre measuring flask and made volume. 100 c.c. of the solution are acidified with 5 c.c. of hydro acid (D = 1·10) and treated with 10 c.c. of 10% potassium solution, the iodine separated being titrated with sodium thiosulpha starch paste. The difference in c.c. between the volumes of dichr and thiosulphate, multiplied by 0·01635, gives the amount of zinc gram of the sample.

⁂

Commercial zinc dust contains 80–90% Zn, 9–10% ZnO, 1·5–2% P small quantities of copper, cadmium, arsenic, antimony, iron, sulphur, carbon, etc., and, sometimes, of calcium and magnesium oxides.

## LEAD AND ITS ALLOYS

Lead is largely used as such and also enters into the composit numerous alloys.

Methods will be given here for the analysis of commercial lead hard lead, alloys of lead with tin and antimony (solder, white antifr metal, white metal for fittings, etc.) being treated under tin and its

### LEAD

The analysis of commercial lead consists in determining the imp present (silver, copper, bismuth, cadmium, arsenic, antimony, iron, cobalt, zinc and manganese). These impurities are, however, pres very small proportions (refined lead contains, indeed, 99·96–99·99% and it is therefore necessary to employ large quantities of the samp to conduct all the analytical operations with the greatest precision.

In a 1·5-litre beaker, 200 grams of the metal are gently heated mixture of 500 c.c. of nitric acid (D 1·2) and 500 c.c. of water. After ing for about 12 hours, the liquid is filtered, the insoluble residue antimonate) being collected on a small filter, washed, placed in a por crucible and kept apart (residue *a*).

The filtrate is treated with 62–63 c.c. of concentrated sulphuri and left to cool and settle, the clear supernatant liquid being sip into a 3-litre beaker. The residue is shaken with 200 c.c. of water ac with nitric acid, allowed to settle and the supernatant liquid added first solution ; to ensure complete washing, this operation should be rep ie filtrate is added to the alkaline sulphide solution and the for the determination of the *antimony* and *arsenic* (*see* 3); on ie other impurities remain as sulphides.

:ipitate thus obtained is dissolved in nitric acid (1 vol. of nitric ·2, and 2 vols. of water) and the liquid evaporated with a slight phuric acid to eliminate the small quantities of lead still present l the nitric acid (excess of sulphuric acid is necessary to keep in solution); the residue is taken up in a little water, filtered with hydrogen sulphide. *Bismuth, silver, cadmium* and *copper* e precipitated (*see* 1), whilst *nickel, cobalt, iron, zinc* and *man-* in in solution (*see* 2).

**rmination of the Bismuth, Silver, Cadmium and Copper.** ides precipitated with hydrogen sulphide are dissolved in nitric e solution evaporated in presence of sulphuric acid.

ERMINATION OF THE BISMUTH. The residue is dissolved in a almost neutralised with pure sodium hydroxide, treated with onate in slight excess and with a little potassium cyanide and ed. If bismuth is present, a white precipitate is obtained, this d off, well washed and dissolved in a little nitric acid. The hen precipitated with a slight excess of ammonia, the precipi- vashed and dissolved in nitric acid and the solution evaporated orcelain crucible; the residue is ignited gently and weighed: 965 = Bi.

ERMINATION OF THE SILVER.[1] The filtrate from the treatment carbonate and potassium cyanide is treated with a little more yanide and a few drops of sodium sulphide, the silver and cad- precipitated as sulphides, while any copper present remains The precipitate is collected, washed, dissolved in nitric acid er precipitated as chloride by addition of a few drops of dilute acid: $\mathrm{AgCl} \times 0{\cdot}7526 = \mathrm{Ag}$.

ERMINATION OF THE CADMIUM. The filtrate from the silver evaporated almost to dryness and treated at the boiling point carbonate. The precipitate formed is collected, washed with lissolved in a little nitric acid, evaporated in a tared porcelain ntly ignited and weighed: $\mathrm{CdO} \times 0{\cdot}8754 = \mathrm{Cd}$.

ERMINATION OF THE COPPER. The filtrate from the silver and lphides (*see b*) is treated with a little sulphuric and nitric acids drops of hydrochloric acid and evaporated to dryness. The issolved in water and the copper determined electrolytically or ally.

---

er is more exactly determined directly by cupellation (*see* Silver and its

containing a few drops of ammonium sulphide and treated on th
with a mixture of 5 parts of saturated hydrogen sulphide solution
part of hydrochloric acid (D 1·2). The iron, zinc and manganese sul
are dissolved and these metals are determined as in (*b*) and (*c*) ;
and cobalt sulphides remain on the filter and are determined as in (*a*

(*a*) DETERMINATION OF THE NICKEL AND COBALT. The nick
cobalt sulphides, which have remained undissolved, are ignited and w
as oxides, which are then dissolved in aqua regia, the solution re
alkaline with ammonia, and the nickel precipitated with dimethylgly
(*see* Argentan).

(*b*) DETERMINATION OF THE IRON. The hydrogen sulphide is e
by boiling from the hydrochloric acid solution containing the iro
and manganese, oxidation being effected by a few drops of nitric ac
the liquid made alkaline with ammonia. The precipitated ferric hyd
is collected, washed and dissolved in hydrochloric acid, the iron bein
reprecipitated with ammonia and weighed as ferric oxide : $Fe_2O_3 \times$
= Fe.

(*c*) DETERMINATION OF THE ZINC. The filtrates from the iron p
tate are together rendered alkaline with ammonia and treated in a
with 2–3 c.c. of ammonium sulphide, the flask being then filled with
stoppered and left for 24 hours. The zinc and manganese sulphid
then collected, washed and treated on the filter with dilute acetic
which dissolves only the manganese sulphide. The residue, consist
zinc sulphide, is dissolved on the filter by dilute hydrochloric acid a
solution evaporated to dryness in a tared crucible. The residue is
with an aqueous suspension of a little pure mercuric oxide free from
evaporated to dryness, heated gently over a naked flame to elimina
mercury, ignited over a blowpipe flame and weighed : $ZnO \times 0{\cdot}8034$

(*d*) DETERMINATION OF THE MANGANESE. The acetic acid solut
the manganese is concentrated and treated with ammonia and hy
peroxide to precipitate the manganese, the precipitate being coll
washed, dried, ignited and weighed : $Mn_3O_4 \times 0{\cdot}7203 = Mn$.

**3. Determination of the Arsenic and Antimony.**—(*a*) DET
NATION OF THE ARSENIC. The alkaline sulphide solution obtain
described on p. 245 is acidified with acetic acid and heated for 3–4
on the water-bath, the arsenic and antimony sulphides and sulphur
separate being filtered off. The precipitate is washed with sat
hydrogen sulphide solution slightly acidified with acetic acid, dried,
from sulphur by means of carbon disulphide, filtered, and the arseni
antimony sulphides dissolved in hydrochloric acid and potassium ch
The liquid is filtered through a small filter, and the filtrate treated

sium ammonium arsenate is collected on a filter, transformed into pyroarsenate and weighed: $Mg_2As_2O_7 \times 0·4827 = As$.

ERMINATION OF THE ANTIMONY. The filtrate from the magnonium arsenate is treated with ammonium sulphide and acidified h sulphuric acid. The antimony is thus precipitated as sulphide, ssolved in ammonium sulphide, the solution being evaporated oorcelain crucible, oxidised with nitric acid, calcined gently and $Sb_2O_4 \times 0·7898 = Sb$.

⁂

ned lead of commerce, especially that destined for making electrical plates, is a very pure metal, containing 99·96–99·99% Pb.

npositions of samples of lead of different origins are as follows Hollard, Hampe):

TABLE XXIX

**Composition of Samples of Lead**

| | Pb | Sb | Ag | Cu | Zn | Fe | Bi | As | Cd | Ni | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| . . | 99·9915 | 0·0050 | 0·001 | 0·0003 | 0·0006 | 0·0016 | — | — | — | — | — |
| . . | 99·9937 | 0·0013 | 0·0006 | — | 0·00085 | 0·0014 | 0·0021 | — | — | — | — |
| inia) | 99·99 | 0·0030 | 0·0010 | 0·0005 | 0·0021 | 0·0047 | 0·0007 | — | — | — | — |
| Lead . . | 99·9924 | 0·0012 | 0·0002 | 0·0002 | 0·0007 | 0·0017 | 0·0030 | — | — | — | 0·0002 |
| . . | 99·9852 | 0·0044 | 0·0006 | 0·0007 | 0·0005 | 0·0011 | 0·0073 | — | trace | trace | — |
| a) . | 99·989 | 0·003 | — | trace | Zn,Ni,Co<br>0·005 | 0·012 | 0·091 | — | — | — | — |
| . . | 99·9575 | 0·0040 | trace | 0·0018 | 0·0002 | 0·0015 | 0·0350 | trace | trace | — | — |

## HARD LEAD

ead or antimonial lead is an alloy of lead and antimony conall quantities of copper and tin and sometimes also iron, nickel, arsenic, etc., and serves for making type, the plates of certain ectric accumulators and cast ornamental articles, and as antital, etc.

ential determinations to be made on these alloys for a complete *e B*) are those of the lead, antimony, copper and tin, determinaon, nickel, arsenic, etc., not being always necessary. Often, terminations of certain elements only are required (*see* Partial

**2. Direct Determination of the Tin.**—From 2 to 4 grams
sample in fine filings are heated to boiling, in an inclined long-necke
covered with a funnel, with 20 c.c. of conc. sulphuric acid until th
sulphate separating appears perfectly white. The cold mass is
with 2–3 grams of tartaric acid dissolved in a little water and the
introduced quantitatively into a 100 c.c. measuring flask, made up to v
mixed and filtered through a dry, pleated filter. 50 c.c. of the
are rendered alkaline with ammonia, heated gently with 5 grams of
acid and the clear solution treated with 5 grams of ammonium o
diluted to about 150 c.c. and kept gently *boiling* during the pass
hydrogen sulphide to precipitate the antimony and copper. After
an hour, the liquid is allowed to cool a little and filtered, 1% oxal
solution saturated with hydrogen sulphide being used for washing.

The filtrate is boiled for a short time with 30 c.c. of hydrochlor
and 20 grams of ammonium oxalate to expel the hydrogen sulphide.
being allowed to cool somewhat, the liquid is treated with a few d
hydrogen peroxide, heated a short time, made up to about 300 c.c.,
to 50–60° and electrolysed—turbid with sulphur as it often is—to
mine the tin: coppered Winkler cathode, spiral Winkler anode,
= 1 amp., temperature about 50°, duration (0·1–0·3 gram Sn) 4–5

Since the antimony and copper sulphides precipitated may retai
amounts of tin, for an exact analysis the precipitation should be
out twice. These sulphides are, therefore, dissolved in the hot in a n
of 10–15 c.c. of conc. hydrochloric acid, 10–15 c.c. of 10% amm
chloride solution and a few crystals of potassium chlorate, the s
being diluted with a little water, filtered, rendered alkaline with am
treated with 5 grams of oxalic acid and 5 grams of ammonium c
diluted to 100 c.c. and subjected at the boiling point to a current of hy
sulphide. After about an hour, the liquid is filtered and the prec
washed with the oxalic solution saturated with hydrogen sulphide
two filtrates are united and the solution—concentrated if necess
an aliquot part of it used for the electrolytic determination of the

## *B.* Complete Analysis

In a 250 c.c. measuring flask, 2·5 grams of the sample in fine
are gently heated with 15 c.c. of water and 10 grams of powdered
acid until the latter dissolves, 4–5 c.c. of nitric acid being added gr

cooled in a desiccator and weighed: $PbSO_4 \times 0{\cdot}6831 = Pb$.

**rmination of the Antimony.**—The 50 c.c. of solution taken ted to 20–30 c.c., neutralised with 50% sodium hydroxide excess of 3–4 c.c. of the latter and 30 c.c. of sodium sulphide 1·225) added and the liquid heated and, after some time, filtered he copper sulphide, etc., directly into a tared Classen capsule; te is washed with hot water in which a little sodium sulphide The filtrate is treated with 50 c.c. of sodium sulphide and f pure potassium cyanide, mixed and electrolysed to determine y, $ND_{100} = 0{\cdot}15–0{\cdot}18$ amp., voltage = 1–1·2, duration (0·1– b) 15–18 hours. When the deposition is complete, the capsule thoroughly washed with water, alcohol and ether, dried at 70° l.

**rmination of the Tin and Copper.**—The 100 c.c. of solution dered slightly alkaline with ammonia, treated with 5 grams d, heated to obtain a clear solution, treated with 7 grams of oxalate, and kept boiling for about an hour while a stream of lphide is passed to precipitate the antimony and copper. When as cooled somewhat in the current of hydrogen sulphide, it is a half-litre beaker, the filter being washed with a hot 1% oxalic n saturated with hydrogen sulphide.

RMINATION OF THE TIN. The filtrate is treated with 30 c.c. rochloric acid and 20 grams of ammonium oxalate and boiled time to expel hydrogen sulphide. After the liquid has cooled few drops of 30% hydrogen peroxide are added and the solu- for a little while, made up to 300 c.c., cooled to 40–45° and— with sulphur—electrolysed to determine the tin: coppered hode, spiral anode, $ND_{100} = 1$ amp., voltage = 3–4, tempera- o°, duration (0·1–0·3 gram Sn) = 4–5 hours (*see also* Elec- ermination of Tin in Ordinary Bronzes).

RMINATION OF THE COPPER. The precipitated copper and lphides, which have been filtered off, are heated gently with hydroxide solution and filtered, the filter being thoroughly n water faintly alkaline with sodium hydroxide; the copper nains undissolved. The filter-paper and precipitate are dried ish, the filter incinerated, the residue dissolved in nitric acid, per determined in this solution by the usual method (*see* Deter- Copper in Ordinary Brass).[1]

**rmination of the Iron, Nickel and Zinc.**—5 grams of are treated with nitric acid (D = 1·2), the solution being left r-bath for a short time and then filtered; the filtrate is treated

⁂

Hard lead contains variable quantities of antimony (usually 1 and may contain small amounts of copper, tin, iron, nickel, arsenic, etc.

The following table contains the results of analysis of samples of ha obtained directly, from ores of lead and antimony (Schnabel):

TABLE XXX

**Composition of Hard Leads**

| Source. | | Pb | Sb | Cu | As |
|---|---|---|---|---|---|
| Oberharz | I | 81·71 | 17·69 | 0·62 | — |
| | II | 82·44 | 16·90 | 0·68 | — |
| | III | 82·08 | 17·34 | 0·62 | — |
| Freiberg | | — | 15 | — | 2·5 |

# ANTIMONY AND ITS ALLOYS

Owing to its brittleness, antimony is rarely used as such, but it part of many industrial alloys, such as white bearing metals, type met

Methods for determining the impurities commonly accompanyin mercial antimony are therefore described, since the value depends purity.

Lead-antimony alloys are treated under lead, while alloys of an with tin alone or with tin and lead together (white metals) are dea along with tin.

## ANTIMONY

Analysis of commercial antimony is generally limited to the dete tion of its commoner impurities: lead, bismuth, copper, iron, arse sulphur.

10 grams of the finely powdered sample are treated with aqu (140 c.c. HCl, 20 c.c. $HNO_3$) diluted with an equal volume of wat solution thus obtained being treated with 60–70 c.c. of 50% tartar solution, then made alkaline with concentrated sodium hydroxide s and subjected to a current of hydrogen sulphide. The separation sulphides is facilitated by heating on a water-bath, the precipitate

e determination of lead in ordinary brasses (*see* p. 226).

**mination of the Bismuth.**—The liquid freed from lead eated to expel the alcohol and treated with hydrogen sulphide e the bismuth and the copper. The precipitate is filtered off, hydrogen sulphide solution acidified with a few drops of sul- and dissolved in a little nitric acid (D 1·2). The solution is n presence of sulphuric acid, taken up in a little water, neu- ost completely with sodium hydroxide, and heated gently t excess of sodium carbonate and a little potassium cyanide. precipitate thus obtained is collected on a filter, washed, nitric acid and again precipitated with ammonia under the dicated for the determination of bismuth in lead.

**mination of the Copper.**—The filtrate from the bismuth— ent with sodium carbonate and potassium cyanide (*see* 2)— vith nitric acid and a few drops of sulphuric acid, evaporated aken up in hot water and the copper in the solution determined l methods.

**mination of the Iron.**—The filtrate obtained after removal th and copper as sulphides (*see* 2) contains all the iron, which d by expelling the excess of hydrogen sulphide, oxidising with nd precipitating with ammonium chloride and ammonia.

**mination of the Arsenic.**—*See* Determination of Arsenic in

**mination of the Sulphur** (Hollard and Bertiaux).—5 sample are treated with nitric acid to which sufficient hydro- is added to give a clear solution. The liquid is evaporated to en up again in nitric acid and evaporated several times with expel the hydrochloric acid completely. The residue is finally water faintly acidified with nitric acid and the solution filtered due washed with water. To the filtrate sufficient ammonia redissolve the antimony oxide at first separating, excess of eing then added and the liquid filtered. In the clear solution acid, formed by oxidation of the sulphur in the sample, is by means of barium nitrate.

⁂

al antimony generally contains small quantities of lead, copper, and, sometimes, bismuth, nickel and cobalt. Pure antimony ite, but the commercial metal has a slightly bluish tint owing to present. It exhibits a marked tendency to crystallise and, indeed, crystalline structure, which is manifested even on the outside by resembling fern leaves, these being regarded—not always with

TABLE XXXI

Results of Analyses of Antimony

| Origin. | | Sb | Cu | Fe | Pb | As | Bi | S |
|---|---|---|---|---|---|---|---|---|
| Hungary (Liptau) | | 98·27 | 0·54 | 0·63 | — | — | 0·36 | — |
| California | I | 98·34 | 0·021 | 0·144 | 0·410 | 1·008 | — | 0·064 |
| | II | 99·081 | 0·052 | 0·039 | 0·538 | 0·036 | — | 0·254 |
| Of various origins (analysis by Hilmy) | I | 98·98 | 0·01 | 0·35 | 0·34 | 0·09 | — | 0·23 |
| | II | 98·87 | 0·02 | 0·16 | 0·73 | 0·09 | — | 0·11 |

# TIN AND ITS ALLOYS

Tin is one of the most important metals, being largely used as su also as a constituent of numerous industrial alloys.

Methods will be given here for the determination of elements oc in commercial tin as impurities, for the analysis of tin-plate and th important tin alloys (phosphor-tin, solder, white antifriction metal metal and metal for fittings).

Alloys of tin with copper (bronzes) are considered along with

## TIN

Commercial tin is usually contaminated by small quantities c copper, iron, bismuth, antimony, sulphur, and arsenic and sometime of molybdenum, tungsten, zinc, manganese, nickel, chromium, etc more important determinations are those of lead, bismuth, coppe antimony, arsenic and sulphur, qualitative tests for the other el being sufficient.

**1. Determination of the Lead, Bismuth, Copper and I** According to the greater or less degree of impurity, from 10 to 2c of the sample, flattened on an anvil or in a small rolling mill and fine, are heated gently on a water-bath with aqua regia (1 vol. c acid with 5 vols. of hydrochloric acid; 10 grams of the sample requ c.c., and 20 grams, 180 c.c.). When the metal is completely attack liquid is allowed to cool and treated, according to the weight of taken, with 25–35 grams of tartaric acid; the latter is dissolved by in Ordinary Brass).

RMINATION OF THE BISMUTH AND COPPER. The alcohol is the liquid separated from the first lead sulphate precipitate nuth and copper precipitated with hydrogen sulphide and ıs in the analysis of antimony.

RMINATION OF THE IRON. The iron is determined as oxide c from the bismuth and copper sulphides (*see* Determination ntimony).

**mination of the Antimony.**—10 grams of the sample are 100 c.c. of hydrochloric acid (D 1·124) and potassium chlorate, eliminated by boiling, the volume made up to about 250 c.c., e liquid is heated on the water-bath, 6 grams of pure reduced ı small quantities to displace the copper and antimony. The etals, together with the small amount of undissolved iron, ff and washed on the filter with dilute hydrochloric acid until o longer gives the reaction for tin with mercuric chloride. The etals are then dissolved in hydrochloric acid and potassium excess of chlorine expelled by boiling, the copper and antimony with hydrogen sulphide and the precipitate well washed and 30 c.c. of sodium sulphide solution (D 1·225) to dissolve the phide. The liquid is filtered directly into the Classen dish, ed with 50 c.c. of the sodium sulphide solution, and the filtrate, tion of 5-6 grams of potassium cyanide, electrolysed to determony (*see* Determination of Antimony in Hard Lead).

**nination of the Arsenic.**—(*a*) 10 grams of the sample in a solution of 100 grams of ferric chloride in 100 c.c. of water, c. hydrochloric acid being added and the arsenic distilled in way (*see* Determination of Arsenic in Iron).

ms of the sample are dissolved in hydrochloric acid contain-ı chlorate, the chlorine being expelled by boiling, and the ixed with one-third of its volume of conc. hydrochloric acid ı sulphide passed through it for some hours. The arsenic precipitated is filtered off on an asbestos filter (Gooch crucible), conc. hydrochloric acid and then with boiled water and dis-nonia; the solution is evaporated in a dish and the residue conc. nitric acid, made strongly alkaline with ammonia and ecipitated with magnesia mixture and alcohol. The precipi-ed, washed, transformed into pyroarsenate and weighed.

**mination of the Sulphur.**—*See* Determination of Sulphur in

*

together, or more than 0·01% of bismuth, or more than 1% of total im

The compositions of tins of different origin are as follows (Hollard, Sch

### Table XXXII

### Composition of Samples of Tin

| Source. | | Sn | Pb | Fe | Cu | Bi | Sb |
|---|---|---|---|---|---|---|---|
| Straits Settlements | Banka | 99·961 | 0·014 | 0·019 | 0·006 | — | — |
| | Malacca | 99·805 | — | 0·020 | 0·072 | — | 0·060 |
| | Pulo Brani | 99·76 | 0·02 | 0·14 | — | — | 0·07 |
| China (Hong-Kong) | | 98·928 | 0·833 | 0·037 | 0·040 | — | 0·044 |
| England | | 99·76 | — | trace | 0·24 | — | — |
| Germany | I | 99·336 | — | — | 0·480 | 0·060 | 0·545 |
| | II | 99·594 | — | trace | 0·406 | — | — |

## TIN-PLATE

With commercial tin-plate the most important determinatio made is that of the tin, the thickness of the layer of this metal dete the value; next comes the determination of the lead, which gives cation of the quality of the tin used. For these two determinatio

Sometimes, however, for certain purposes (hygienic, for instanc mination of the lead alone is of interest, it being desired to ascerta tinning has been done with commercial tin or with an alloy of lead The determination of the lead alone is described in 2.

**1. Determination of the Tin and Lead.**—From 1 to 2 sq. the tin-plate[1]—taken from the middle of the plate, since the ti often irregular at the edges—is measured exactly, de-fatted with benzene and weighed, so that the results may be referred to the w well as the surface of the sample. The measured portion is cut in squares of 1–2 cm. side, these being heated to boiling for 5 minu covered beaker with 50 c.c. of 10% hydrochloric acid (25–30 c hydrochloric acid diluted to 100 c.c. with water). The hydrochl solution is decanted into a 300 c.c. measuring flask and the met for 5 minutes with another 50 c.c. of the acid, this being decanted if necessary, the residue treated a third time; the colour of the met be a uniform iron-grey when all the tin is dissolved. Tin and easily dissolved in the hot by hydrochloric acid of this concentratio

ting electrodes. 100 c.c. of the filtrate are treated in a
aker with 20–30 c.c. of 40% sodium sulphite solution to
polysulphides, made up to about 200 c.c. and electrolysed at
ered and then tinned Winkler cathode[2]; spiral anode, 1000
inute; temperature, 60°; $ND_{100}$, 3–3·5 amp.; voltage, 5–6;
5–20 minutes.

ie electrolysis is complete, the rotation of the anode is sus-
without interrupting the current, the electrolytic beaker replaced
l with water; after some time, the cathode is detached, washed
with water, alcohol and ether, dried at 70° and weighed. The
d, multiplied by 3, gives the tin contained in the sample taken.
tating electrodes are used, the determination of tin in tin-plate
longer than an hour.

onary electrodes. In a ½-litre conical flask, 100 c.c. of the
phide filtrate are treated, under a draught hood, with a little
cyanide to reduce the polysulphides, and hydrochloric acid
an equal volume of water added until the reaction is acid, the
kept covered with a funnel and shaken meanwhile. When
f gas ceases, the liquid is boiled for some time with 25 c.c. of
chloric acid to dissolve the tin sulphide which separates and
the sulphur. After addition of 25 grams of ammonium oxalate
to 250 c.c., the liquid is electrolysed: coppered Winkler cathode;
iral anode; $ND_{100} = 1$ amp.; voltage $= 3–4$; temperature,
on (for 0·1–0·5 gram Sn), 4–5 hours (*see also* Electrolytic Deter-
Tin in Ordinary Bronzes). Multiplication by three of the tin
the amount in the sample taken.

*metrically*. In a ½-litre conical flask, 50 or 100 c c. of the alkaline
rate (*see* I, p. 254) are diluted with water and acetic acid added
action is faintly acid, the tin being thus precipitated as sulphide.
ing overnight, the precipitate is filtered off, washed with 10%
acetate solution and dried at 100–120°. The filter and precipitate
ced into a tared porcelain crucible, the filter-paper incinerated
on of a few crystals of ammonium carbonate and then ignited
tannic sulphide is completely converted into the white oxide
d: $SnO_2 \times 0·7881 = Sn$.

---

ence of copper it is convenient to use sodium sulphide, but in such case
termination of the tin with rotating electrodes cannot be carried out.
coppering of the electrode, *see* p. 225. For the subsequent tinning, the
ition is employed: 3–4 grams of stannic ammonium chloride are dissolved
cold water to which are added 150 c.c. of saturated ammonium bioxalate
ie cathode is immersed in this solution and the current passed for some
$D_{100} = 0·2–0·5$ ampere.

nium or sodium sulphide, and the filter and precipitate heated to with 15–20 c.c. of nitric acid (D 1·2) in a small covered beaker. The s is decanted through a filter and the residue boiled with 20–30 c.c. following mixture, which dissolves also any small amount of lead s formed by oxidation of the sulphide: 40 c.c. of ammonia (D 0·923), of nitric acid (D 1·332) and 5 grams of copper nitrate. The liquid is the filter washed with hot water acidified with nitric acid, and the made up to about 200 c.c. and electrolysed to determine the lead: cathode; matte gauze cylinder anode; ND = 0·3 amp.; voltage (*see also* Electrolytic Determination of Lead in Ordinary Brass).

When the deposition of the lead is complete, the anode is wash water alone, dried at 200–220° and weighed: $PbO_2 \times 0{\cdot}866 = Pb$

2. *Gravimetrically*. The lead and iron sulphides (*see* 1, p. 255) filter are well washed with water containing a little ammonium s dissolved in nitric acid (D 1·2) and filtered by decantation. The is again boiled twice with nitric acid and finally washed with water a with nitric acid. The nitric acid solution is evaporated with sulphu until white fumes appear, and the residue, when cold, taken up in the lead being determined as sulphate as in the case of tin.

**2. Determination of the Lead alone.**—The surface of the ti is scraped with a penknife so that as little as possible of the metal neath is removed, about 1–1·5 gram of thin shavings being obtaine particles of iron are removed with a magnet. The shavings are m a covered beaker with 6 c.c. of fuming nitric acid (D 1·5), 3 c.c. o being poured carefully down the side of the beaker so that the two mix slowly and the action proceeds regularly. At the end of the the liquid is heated to boiling, diluted with 50 c.c. of boiling wat when the liquid above the metastannic acid has become clear, filte decantation through a dense filter and washed by decantation with slightly acidified with nitric acid.

In the filtrate the lead is determined either electrolytically or metrically by the methods given for the analysis of alloys of lead (*see* p. 259). When the lead is separated as peroxide or sulphate, t unavoidably present is determined in the residual liquid by precip with ammonium chloride and ammonia. Deduction of the weight found from the total weight of the shavings gives the amount of l alloy taken for analysis, and to this the quantity of lead found is re

⁂

-bronzes, includes :

**rmination of the Phosphorus.**[1]—The alloy is treated with
: acid and the phosphorus thus liberated as hydrogen phosphide,
dised with bromine water and determined as phosphoric acid.
*is.* A flask of about 500 c.c. capacity furnished with a stopper
ich pass (1) a tapped funnel for the introduction of the hydro-
and (2) two tubes bent at right angles, one reaching almost
om of the vessel and serving for the introduction of a stream
oxide into the apparatus, and the other to collect the gas evolved
reaction. The latter tube communicates with three absorption
containing bromine water and a small quantity of bromine
ne millimetres deep) and the third bromine water alone.
*e.* 2–5 grams of the alloy in small fragments are introduced
sk and the latter stoppered and connected with the washing
rrent of carbon dioxide being passed for about five minutes to
r. From 50 to 100 c.c. of concentrated hydrochloric acid are
little by little, and when the attack is complete the liquid is
oiling, and a current of carbon dioxide again passed to drive
ducts of the reaction. The contents of the three bottles are
a beaker, the excess of bromine eliminated by boiling and the
acid precipitated either (1) as magnesium ammonium phosphate
standing, is filtered off, dried, ignited strongly and weighed :
0·2787 = P,[2] or (2) with ammonium molybdate (*see* Iron, 4).

**rmination of the Tin.**—The hydrochloric acid solution is
a 500 c.c. measuring flask and made up to volume. An aliquot
ponding with 0·5–0·75 gram of the sample, is rendered alkaline
nia, the precipitate redissolved by addition of a little oxalic acid
iid boiled for a short time with 25 c.c. of hydrochloric acid, 25
monium oxalate and a few drops of hydrogen peroxide, made
: 250 c.c. and electrolysed at 40–50° to determine the tin (*see*
Determination of Tin in Ordinary Bronzes).

⁂

ial phosphor-tin or tin phosphide usually contains about 4% of
The brand marked N.0 contains about 5% P and N.1, 2·5%.
icts, however, contain only 1% or even less.

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mell and S. L. Archbutt, *Journ. Soc. Chem. Industry*, 1908, XXVII, p.

ample contains arsenic, magnesium ammonium arsenate is precipitated
nesium ammonium phosphate. In this case the weighed precipitate is
hydrochloric acid, the solution reduced with sulphur dioxide and the

# ALLOYS OF LEAD AND TIN

The lead-tin alloys are used for *soldering* and for many other p such as making ornamental articles, statuettes, toys, tubes for pa perfumery, tin-foil, etc.

In these alloys, the essential determinations are those of the l tin (*see* 1). Sometimes, however, for special products, the deter of the lead alone or of the tin alone is of interest (*see* 2), whilst cases, determination of the impurities (Cu, Sb, As, etc.) is desired (*s* Metals).

**1. Determination of the Lead and Tin.**—About 1 gram of t as filings is treated in a covered beaker with 6 c.c. of fuming ni (D = 1·5) and 3 c.c. of water then poured carefully down the sid beaker so that the two liquids mix slowly and the action procee and regularly. When the action is complete, the liquid is heated t diluted with 50 c.c. of boiling water, and, when the liquid above cipitated metastannic acid has become clear, filtered by decantation a close filter-paper. The precipitate is washed by decantation wi slightly acidified with nitric acid, collected on the filter, washed water [1] and treated as in *B*. The filtrate is utilised as in *A*.

*A*. DETERMINATION OF THE LEAD.

1. *Electrolytically*. The filtrate is made up to volume and a part, containing about 0·2–0·25 gram of lead, is treated with 1- of pure copper dissolved in 10–15 c.c. of nitric acid, diluted to 200- and electrolysed at the ordinary temperature: Winkler anode; cy gauze cathode; $ND_{100}$ = 0·3 amp.; voltage = 2–2·2; and duratio hours.

When by raising the level of the liquid the deposition of the lead to be complete—even although copper may still remain in solut electrolytic beaker is replaced by another filled with distilled w current being maintained. After some time the anode coated v peroxide is detached, washed with water *alone* and dried at 200–22 factor for converting weight of peroxide into that of lead is 0·8 or 0·8635 according as the amount of the peroxide is less than c between 0·1 and 0·3 gram, or above 0·3 gram (Classen).

2. *Gravimetrically*. The filtrate is evaporated in presence of of conc. sulphuric acid until white fumes appear. When cold, t is taken up with 50 c.c. of water, heated gently and stirred, allowe and treated with 15 c.c. of 95% alcohol. After 1–2 hours, the lead is collected in a Gooch crucible and weighed (*see* Gravimetric Dete

d 10–15 c.c. of sodium sulphide (D 1·225), the remaining pro-
ıg that given for the electrolytic determination of tin in ordinary
: p. 232).

*imetrically.* The filtered and washed metastannic acid precipi-
d at 100° and removed as far as possible from the filter to a tared
rucible. The filter-paper is incinerated in a dish, the ash added
ipitate, the whole moistened with a few drops of nitric acid, the
cid evaporated and the residue ignited at first with an ordinary
afterwards by means of the blowpipe, and weighed[1]: $SnO_2 \times$
n.

**ermination of the Lead alone or of the Tin alone.**

D ALONE. This is of interest in some tin-lead alloys composed
in, such as solder for culinary utensils and the like.

vered electrolytic beaker of 350 c.c. capacity, 1–3 grams of the
ings are treated, according to the amount of alloy taken, with
f fuming nitric acid (D 1·5), 3–9 c.c. of water being then allowed
wly down the wall of the beaker. When the attack of the metal
, the liquid is boiled for a short time, diluted to about 250 c.c.
ghly mixed with 2–3 grams of copper nitrate or with 1–1·5 gram
per dissolved in a little nitric acid, the metastannic acid being
settle and the liquid, *without filtering*, electrolysed to determine
Winkler cathode; matte gauze cylinder anode; $ND_{100}$, 0·3 amp.
, 2–2·2. The cathode should touch the bottom of the beaker,
anode should not reach to within about 1 cm. from the layer of
(for the factor, Pb : $PbO_2$, *see* p. 258). In this way, even the
tities of lead held by the metastannic acid may be liberated by
t.

ALONE. In other types of alloy, consisting essentially of lead
hard lead) with small quantities of tin (0·5–15%), such as
or tubes for perfumery, colours, etc., wires for electric valves,
of interest to determine the tin alone.

to 3 grams of the sample in filings or clippings are treated with
of boiling conc. sulphuric acid and, when the action is at an end,
diluted somewhat. When the liquid is cold, 5–6 grams of tartaric
ssolved in it and the whole transferred to a 100 c.c. measuring
e up to volume, and filtered through a dry filter. The tin is
l in 50 c.c. of the filtrate in the way given for the determination
ard lead (*see* p. 248).

⁂

nposition of *solder* varies widely with the metals to be soldered and to obtain the shining white colour of tin. With these last two typ tin-foil, the most important determination is that of the tin, this effected as for the tin alone in lead-tin alloys (*see* Alloys of Lead an p. 258). A complete analysis may be carried out by the method ind for the analysis of lead-tin alloys, when these are the only constituent m or by that given for white metal in the case of an alloy of lead, anti and tin.

If the foil is tinned externally, the coating must be removed in that the quantity of tin actually present in the alloy may be detern If the foil is moderately thick, the surface layer may be removed mec cally from the two faces and the quantitative determination made o sample thus prepared. If, however, the foil is too thin and weak scraped, the surface tin is removed by means of sodium hydroxide so and hydrogen peroxide, which, at the proper concentration, easily a and dissolves the layer of tin, whereas the tin in the alloy is acted on not at all or but slightly. The conditions to be observed are as follo

From 5 to 6 grams of the foil are freed from grease by treatment ether, cut into squares of about 1 cm. side and heated in a 200 c.c. with 20 c.c. of 10% sodium hydroxide to 40°, 6–8 drops of 30% (100 vo hydrogen peroxide being then added with continual shaking. The su tin passes rapidly into solution and as soon as the lead-grey colour ass by the pieces of metal indicates that this process is complete, the al solution is decanted off and the residue washed repeatedly with alcohol and ether successively and dried at 60–70°. The foil being freed from the surface tin, the quantitative determination of the compo of the alloy is carried out by the methods indicated above.

## WHITE METAL

This includes many types of alloys with a basis of tin-antimony, antimony or lead-tin-antimony, together with small quantities of c and sometimes zinc and iron (rarely mercury and arsenic), used as antifr metals, type metal, metal for fittings, etc. The composition therefore the analytical methods to be used, vary with the purp the metal. Three groups may be distinguished:

(1) *Alloys with a basis of tin* (70–85%) and *antimony* (10–15%), a little copper (5–10%) and lead (0·5–2%), and perhaps zinc and

(2) *Alloys with a basis of lead* (60–80%), *antimony* (10–15%) ar (10–25%), with a little copper (0·5–1%) and perhaps zinc, iron and ar

(3) *Alloys with a basis of lead* (75–90%) and *antimony* (10–25%)

group the method of analysis will be described later, but rtain purposes only the content of copper or tin is of interest, ethod is given which permits of the direct and moderately rapid on of each of these elements.

**t Determination of the Copper.**[1]—In a 200 c.c. measuring ns of the alloy are heated gently with 20–25 c.c. of nitric acid hen the action is complete, the nitrous vapours are eliminated ling and the liquid cooled, treated with 3 c.c. of conc. sulphuric cooled, diluted somewhat, rendered alkaline with ammonia, 15–20 c.c. of 10% sodium phosphate solution and made up and mixed. After standing, the liquid is filtered through a nd 100 c.c. of the filtrate neutralised with nitric acid, treated f conc. nitric acid and 20 c.c. of 10% sulphuric acid, and elec- Vinkler cathode; spiral Winkler anode; $ND_{100} = 0{\cdot}2$ amp.; ·8–2·2; and duration, 10–12 hours.

ne copper is completely deposited, the electrolytic beaker is another small beaker full of distilled water acidified slightly ric acid, the cathode being detached after some time, washed alcohol and ether, dried at 70° and weighed. (Weight of coppe = percentage of copper in the sample.

loy contains arsenic, the copper deposited may have a brown this case the deposit is dissolved in 5–6 c.c. of nitric acid and iluted and again electrolysed.

**t Determination of the Tin.**—According to the supposed 1–3 grams of the alloy in fine filings are treated with 15–20 c.c. ated, boiling sulphuric acid, the subsequent procedure being ed for the direct determination of tin in hard lead (*see* p. 247).

## 1. Alloys with a Tin-Antimony Basis

loys usually contain 70–85% Sn, 10–15% Sb, 5–10% Cu, 0·5– possibly zinc and iron. Their complete analysis is carried out

**trolytically.**[2]—In a conical flask covered with a small funnel, of the alloy in turnings or filings is treated with the least possible aqua regia (10–15 c.c.). When the action is over, 10–15 c.c. ntaining in solution 2–3 grams of tartaric acid are added and nade slightly alkaline with concentrated caustic soda solution with a further quantity of 2 grams of sodium hydroxide and f sodium sulphide solution (D 1·25). T e iq i i heated on trolysed at the ordinary temperature to determine the antimony: Classen capsule cathode; disc or spiral anode; $ND_{100} = 0{\cdot}15–0{\cdot}17$ amp.; voltage $= 1–1{\cdot}2$; and duration = 15–17 hours.

When the whole of the antimony is deposited, the electrolyte is poured into a ½-litre flask and the capsule and disc (or spiral) washed with a little water which is also poured into the flask. The capsule is then thoroughly washed with water, alcohol and ether, dried at 70° and weighed.

2. Determination of the Tin. The alkaline liquid freed from antimony is acidified faintly with dilute sulphuric acid (1 vol. acid, 2 vols. water), the flask being kept under a hood, covered with a funnel and shaken. The liquid is then boiled for some time to expel the bulk of the hydrogen sulphide and cyanogen compounds, left on a boiling water-bath for about 15 minutes and filtered through a filter-paper moistened with ammonium sulphate solution, the precipitate being washed with a little hot water saturated with hydrogen sulphide.

The filter and precipitate are then heated to boiling in a small covered beaker with 20 c.c. of conc. hydrochloric acid and 15–20 c.c. of 10% ammonium chloride solution, a few crystals of potassium chlorate being subsequently added to complete the action. The liquid is then diluted with 15–20 c.c. of boiling water, shaken and filtered into a ½-litre flask, washing with hot water acidified with hydrochloric acid. The filtrate is rendered slightly alkaline with ammonia, treated with 5 grams of oxalic acid and heated a little, 5 grams of ammonium oxalate being added to the clear solution, which is then made up to 150–200 c.c. and subjected to a moderate current of hydrogen sulphide while gently boiling. Under these conditions the traces of copper dissolved in the sodium sulphide and also any arsenic present are precipitated. After about an hour the liquid is allowed to cool somewhat in the stream of hydrogen sulphide and is then filtered into a ½-litre beaker and the filter washed with a hot 1% oxalic acid solution saturated with hydrogen sulphide. The filtrate is boiled with 25 c.c. of conc. hydrochloric acid and 12–14 grams of ammonium oxalate for about 15 minutes to expel the hydrogen sulphide, allowed to cool a little, treated with 3–4 drops of 30% hydrogen peroxide, boiled again, cooled to about 50° and, without removal of any suspended sulphur, electrolysed to determine the tin (*see* Electrolytic Determination of Tin in Ordinary Bronzes).

3. Determination of the Copper and Lead. The filter and hydrogen sulphide precipitate (*see* 2) are incinerated in a small dish and then ignited, the residue being dissolved in 2–3 c.c. of nitric acid.

The sulphides remaining undissolved in the sodium sulphide (*see A*) are dissolved in 10–15 c.c. of boiling nitric acid (D 1·2), filtered by decantation, the residue bein treated again twice with nitric acid and the united

RMINATION OF THE IRON AND ZINC. The liquid from which the
pper have been separated is used for the determination of the c as in ordinary brasses.

RMINATION OF THE ARSENIC. *See* Determination of Arsenic in

**imetrically.**—2 grams of the sample are acted on with sible quantity of aqua regia at a gentle heat on a water-bath. tion is complete, the liquid is diluted with 10–15 c.c. of water 3 grams of tartaric acid in solution, then rendered faintly sodium hydroxide solution and treated with *colourless* sodium ery slight excess. The liquid is heated on a water-bath with aking until the precipitate has settled and is then filtered by hot water containing a little sodium sulphide being used for e filtrate, containing tin and antimony, is analysed according precipitate, containing lead, copper, etc., according to 2.

MINATION OF THE TIN AND ANTIMONY. The filtrate is made and 200 c.c. treated in a ½-litre flask with 6 grams of potassium grams of tartaric acid and slowly and, if necessary, with cooling, % hydrogen peroxide to decolorise the solution, that is, to e sodium sulphide completely into sulphate. The liquid is e time to expel excess of hydrogen peroxide, allowed to cool, ith saturated oxalic acid solution and treated with 5 grams c acid, diluted to about 250 c.c. and subjected at the boiling derate current of hydrogen sulphide for about an hour. The n allowed to cool somewhat in the stream of hydrogen sulphide mony sulphide filtered off and washed with 1% oxalic acid ated with hydrogen sulphide.

antimony sulphide may contain small quantities of tin, it is mixture of 10–15 c.c. of conc. hydrochloric acid and 10–15 nmonium chloride solution, a few crystals of potassium chlorate when the mixture begins to boil. After dilution with water, filtered, made slightly alkaline with ammonia, treated with alic acid, diluted to 150 c.c. and the boiling liquid again treated n sulphide. FILTER

*ination of the tin.* The two filtrates are united, rendered line with ammonia, acidified with acetic acid, and a current sulphide passed through the solution for about three hours. f about 30 minutes on a water-bath to facilitate the separation ate, the latter is filtered off and washed with hydrogen sulphide ining a little ammonium sulphate. The tin sulphide thus ried at 120°, transformed by ignition into the oxide and the evaporated in a tared porcelain crucible, the residue treated careful avoid spurting, with nitric acid and the liquid evaporated to dryness. treatment with nitric acid is repeated twice to ensure the complete oxi of the sulphur, the residue being ignited and weighed: $Sb_2O_4$ × 0·7 Sb.

2. Determination of the Lead, Copper, Iron and Zinc. Th phides remaining undissolved in sodium sulphide are dissolved in acid (D 1·2), the filtered solution treated with a little sulphuric aci evaporated until white fumes appear, the subsequent procedure be indicated for the gravimetric determination of lead, copper, iron an in ordinary brass.

## 2. Alloys with a Lead-Antimony-Tin Basis

These alloys usually contain 60–80% Pb, 10–15% Sb, 10–25% little copper and possibly zinc, iron, arsenic. The complete analy carried out as follows:

*A*. **Electrolytically.**—1 gram of the sample in fine filings is t with 20 c.c. of conc. hydrochloric acid and 2–3 c.c. of conc. nitric ac left overnight in order that the action may proceed slowly but comp

1. Determination of the Lead. The acid solution is treatec 10 vols. of absolute alcohol (220–230 c.c.), cooled and after a suitab (3–4 hours)—when the bulk of the lead chloride has separated (only milligrams, to be estimated later, remain in solution)—filtered thro tared Gooch crucible, washed with alcohol to a neutral reaction, di 100° and weighed: $PbCl_2 \times 0{\cdot}7447 = Pb$.

2. Determination of the Tin, Antimony, Copper, Iron and The alcoholic solution, freed from lead chloride, is evaporated wi grams of tartaric acid until the alcohol is completely expelled, then slightly alkaline with concentrated sodium hydroxide solution and t with 2 grams of sodium hydroxide and 15–20 c.c. of sodium sulphid tion ($D = 1{\cdot}225$). After being heated for about 15 minutes on a bath, the liquid is filtered into a Classen capsule, the precipitate washed five or six times with sodium sulphide solution (60–70 c.c. and then with hot water containing a few drops of sodium sulphide filtrate contains the tin and antimony and the insoluble residue the c traces of lead dissolved as chloride, and any iron and zinc present.

For the electrolytic determination of these elements, the metho viously described (*see* 1, *A*, p. 261)[1] is followed.

*B*. **Gravimetrically.**

c solution is evaporated with 2–3 grams of tartaric acid until is completely expelled, the residue being taken up in water 'd made faintly alkaline with concentrated sodium hydroxide treated with colourless sodium sulphide solution in very slight liquid is heated on the water-bath and filtered, the subsequent ing that for the gravimetric analysis of alloys with a tin-anti- containing a little copper (*see* p. 263).

## 3. Alloys with a Lead-Antimony Basis

oys usually contain 75–90% Pb, 10–25% Sb, and small quan- and copper (0·5–2%). Their complete analysis is carried out iods given for hard lead.

⁂

etals vary in composition according to their uses, the analytical ome of the commoner types being as follows :

TABLE XXXIII

### Composition of White Metal

| Type. | Sn | Pb | Sb | Cu | Fe | Zn |
|---|---|---|---|---|---|---|
| *riction metals :* | | | | | | |
| the Italian Railways . | 83 | — | 11 | 6 | — | — |
| French ,, . | 83·33 | — | 11·11 | 5·55 | — | — |
| Russian ,, | 90<br>78·5 | —<br>— | 8<br>11·5 | 2<br>10 | —<br>— | —<br>— |
| , German ,, . | 83 | — | 11 | 6 | — | — |
| , Austrian ,, . | 82 | — | 12 | 6 | — | — |
| e bearing metal . . | 76·7 | — | 15·5 | 7·8 | — | — |
| etal . . . . . . . | 90–92 | — | 8–9 | up to 3 | — | — |
| *n and fittings metals :* | | | | | | |
| the Italian Railways . | 14 | 76 | 10 | — | — | — |
| , French Northern Railway . . | 12 | 73 | 15 | — | — | — |
| , French Eastern Railway . . . | 12 | 80 | 8 | — | — | — |
| certain German Railways. . . | 42 | 42 | 16 | — | — | — |
| etal' | 5 | 6 | 7 | — | — | — |

# NICKEL AND ITS ALLOYS

Nickel is largely used for nickel plating and for coins of low value, and also occurs in many alloys.

Descriptions will be given here of the tests to be made on commercial nickel and of the analysis of german silver and the like, which are the most important nickel alloys. For the analysis of bronzes containing nickel, *see* Nickel-bronzes.

## NICKEL

The more common determinations involved in the analysis of commercial nickel are those of copper, cobalt, iron, manganese, carbon, sulphur, arsenic and silicon.

10 grams of the sample are dissolved in nitric acid and evaporated in presence of sulphuric acid until dense white fumes appear. When cold the residue is treated with water acidified with sulphuric acid, heated to boiling, filtered and washed with boiling water acidified with sulphuric acid. The residue on the filter is treated according to 1 and the filtrate as described in 2, 3 and 4.

**1. Determination of the Silicon.**—The insoluble residue, consisting of silica and possibly metastannic acid, graphitic carbon, etc., is dried, ignited in a platinum crucible, weighed, treated with hydrofluoric acid and a few drops of sulphuric acid, heated to expel excess of acid, again ignited, cooled and weighed. The loss in weight gives the silica and therefore the silicon (*see* Determination of the Silicon in Iron).

**2. Determination of the Copper.**—The copper is precipitated in the filtrate by means of hydrogen sulphide and is then determined either as oxide or electrolytically by dissolving the sulphide in nitric acid and electrolysing the solution.

**3. Determination of the Nickel and Cobalt.**—(a) *Determination of the nickel.* The filtrate from the copper sulphide is made up to volume in a 500 c.c. measuring flask, and 100 c.c. (corresponding with 2 grams of the sample) evaporated to dryness. The residue is taken up in ammonia and the volume then made up to 100 c.c. with ammonia (D 0·91), 5 grams of ammonium sulphate being dissolved in the liquid and the latter electrolysed to determine the nickel and cobalt together: Winkler cathode; spiral Winkler anode; $ND_{100} = 0{\cdot}7\text{–}1$ amp.; temperature, ordinary, and duration, 15–17 hours.

her in the same Rothe apparatus with dilute sulphuric acid, he cobalt passes. The aqueous layer is separated—washing dilute sulphuric acid—and evaporated to dryness, the residue ıp in a little water, the solution made faintly ammoniacal and f nickel present with the cobalt precipitated with alcoholic xime solution. The precipitate is filtered off, the filtrate a small flask with nitric and sulphuric acids to destroy organic he residual liquid placed in a tared crucible, where the excess s expelled and the remaining cobalt sulphate then weighed : $O_4$ = Co.

**nination of the Iron and Manganese.**—The 400 c.c. of (8 grams of the sample)—quite free from hydrogen sulphide to about 1·5 litre, treated with hydrogen peroxide and made ammonia, heated and then left at rest for a short time on a he supernatant liquid being subsequently siphoned off and ted iron and manganese oxides collected on a filter. The dissolved in a little hydrochloric acid and the precipitation en peroxide and ammonia repeated, the precipitate being er a short rest on the water-bath, washed with slightly ammo- dried, ignited and weighed.

the ferric and manganese oxides together. The iron alone mined either by titration or by separating it as basic acetate.

**nination of the Carbon.**—3 grams of the sample are the water-bath in concentrated copper-potassium chloride carbonaceous residue being collected on an asbestos filter, and burnt in a current of oxygen (*see* Determination of Carbon 68).

**nination of the Sulphur.**—10 grams of the sample are nitric acids, evaporated several times with hydrochloric acid ıken up in water and hydrochloric acid and filtered. In the lphuric acid formed by oxidation of the sulphur is precipitated chloride solution.

**nination of the Arsenic.**—From 10 to 20 grams of the ssolved in nitric acid, the solution evaporated with sulphuric e nitric acid is completely expelled, the residue dissolved in l with 5–10 grams of ferrous sulphate and excess of hydro- nd the arsenic determined by distillation (*see* Determination Iron).

⁂

l nickel is more or less pure according to the processes used to the impurities which it may contain (Cu, Co, Fe, Mn, Sn, Pb, Sb, always present in commercial nickel to the extent of 1–2%, copper, which does not exceed 1%, and the other elements mentioned above, provided these are present only in small proportions, have no deleterious effect on the technical properties of the metal.

The following table gives the properties of samples of nickel of different sources (Lunge, Hollard):

TABLE XXXIV

**Results of Analyses of Nickel**

| Origin. | Ni | Co | Cu | Mn | Fe | Sb | As | Pb | S | C | Si | $SiO_2$ | $Al_2O_3$ | CaO and Alkalies | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| German Cubes I | 97·08 | 0·89 | 0·15 | — | 1·22 | — | — | — | trace | 0·02 | — | 0·35 | 0·12 | trace | — |
| German Cubes II | 98·21 | 1·19 | 0·07 | — | 0·25 | — | — | — | trace | trace | — | 0·24 | trace | trace | — |
| Granules from "Königswarter and Ebell" | 98·58 | 0·75 | 0·10 | — | 0·24 | — | — | — | trace | trace | 0·26 | — | trace | trace | — |
| English cubes | 96·86 | 1·26 | 0·06 | — | 1·05 | — | — | 0·40 | trace | 0·09 | — | 0·10 | trace | trace | — |
| "Landore" cylinders | 97·48 | 1·05 | 0·06 | — | 0·79 | — | — | — | trace | trace | — | 0·38 | 0·22 | trace | — |
| Unknown origin I | 95·17 | 1·71 | 1·13 | 0·91 | 0·58 | — | trace | — | trace | 0·22 | — | 0·16 | 0·03 | trace | — |
| Unknown origin II | 92·58 | 0·94 | 3·77 | 1·49 | 0·31 | 0·04 | trace | — | trace | 0·18 | — | 0·39 | 0·14 | trace | 0·05 |
| French coinage [1] | 97·75 | 1·587 | 0·102 | — | 0·259 | — | — | — | 0·039 | — | — | 0·254 | — | — | — |
| Electrolytic nickel | 99·22 | 0·71 | 0·01 | 0·046 | — | — | 0·006 | — | — | — | — | — | — | — | — |

## GERMAN SILVER

## (Argentan, Packfong, Alfénide)

Owing to their colour and stability, these alloys are used for domestic articles, for ornaments in place of silver, for coinage, etc. They all consist essentially of copper, nickel and zinc, sometimes with small quantities of lead and iron and, in rare cases, tin and manganese. Other alloys of similar appearance, used for coating rifle bullets or for coinage, consist of 70–80% Cu, 20–30% Ni, and small proportions of lead, iron, zinc, etc.

The analysis of german silver and of copper-nickel alloys in general is carried out as follows:

### *A*. Electrolytically [2]

In a small covered beaker, 0·5 gram of the alloy is gently heated on a water-bath with 15 c.c. of nitric acid (D 1·2), the solution being subsequently diluted with 20–30 c.c. of water. Turbidity indicates tin, which is determined as in 1; a perfectly clear liquid is, however, used at once for the determination of copper and lead (*see* 2).

**1. Determination of the Tin.**—The liquid is evaporated to dryness, the residue taken up in a little water and a few drops of nitric acid and the lution is at once diluted to about 150 c.c. and electrolysed for eous determination of the copper and lead (*see* Electrolytic n of the Copper and Lead in Ordinary Brasses, p. 224).

er, the alloy contains tin and the solution is evaporated to parate the metastannic acid, the filtrate is treated with 15 c.c. l (D 1·2), diluted to 150 c.c. and electrolysed.

**mination of the Iron.**—The liquid from which the copper e been separated, together with the wash water from the first aporated until white fumes of sulphuric acid appear, in order he nickel and zinc nitrates into sulphates ; the 10% sulphuric added to the electrolyte is sufficient for this purpose. When due is taken up with water acidified with sulphuric acid and water-bath, the clear solution being treated with a few drops peroxide and made alkaline with ammonia. After a short water-bath, the precipitate is filtered off, dried, ignited and $_2O_3 \times 0{\cdot}6994 = Fe$.

**nination of the Nickel.**—The filtrate from the ferric hy- ade up to about 150 c.c. and then mixed with 30 c.c. of con- monia and 0·1 gram of hydroxylamine sulphate, the electrodes ed but the circuit not closed. A thermometer is fitted and overed with the two halves of a clock-glass having gaps for the electrodes and for the thermometer and heated to 90°. lrops of fresh concentrated sodium sulphite solution are then electrolysis immediately started, the temperature being kept and occasional small quantities of ammonia (1 vol. conc. 1 vol. water) added from a wash-bottle to replace that lost heating : Winkler cathode ; spiral Winkler anode, $ND_{100} =$ voltage = 2 ; temperature = 90° ; duration (0·1 gram Ni) s.

liquid changes from blue to colourless, a drop of it is with- reated with alcoholic dimethylglyoxime solution to ascertain is completely deposited. When this is the case, the flame is the thermometer taken out and washed, the cover removed rolytic beaker replaced by another filled with distilled water. me the cathode is detached, washed with water, alcohol and at 70° and weighed.[1]

**mination of the Zinc.**—In the liquid from which the nickel noved, mixed with the wash water contained in the beaker ated to about 150 c.c., the zinc is determined by one of the cated for the electrolytic determination of zinc in ordinary ). 224).

**2. Determination of the Nickel.**—The slightly ammoniacal from which the ferric hydroxide has been separated is treated with excess (about 50 c.c. of reagent are required per 0·1 gram nickel) alcoholic solution of dimethylglyoxime. The solution is heated for 30 minutes on the water-bath and—after the completion of the precipi has been ascertained by pouring a fresh quantity of the reagent dow sides of the beaker—filtered through a tared Gooch crucible, which peatedly washed with hot water, dried at 120° and weighed: (wei the nickeloxime) × 0·2032 = nickel.

**3. Determination of the Zinc.**—The filtrate from the nickel preci is evaporated on a water-bath with nitric and sulphuric acids to elir the excess of alcohol and destroy the excess of dimethylglyoxime. residue is taken up in water, the solution neutralised exactly with am and treated with 8–10 drops of 2N-hydrochloric acid, and the zin cipitated as in the gravimetric analysis of ordinary brasses.

**4. Determination of the Cobalt.**—The liquid freed from zinc su is evaporated to 50–60 c.c., neutralised with ammonia and treated at with a current of hydrogen sulphide. The cobalt is precipitated as sul which is converted into sulphate and the latter weighed.

Some types of argentan contain also silver (3–10% or even more). case, the silver is precipitated as chloride before the copper is determin Determination of Silver in Commercial Copper). The filtrate from the chloride is evaporated in presence of nitric acid to expel excess of hydro acid, the residue being dissolved in water and treated subsequently as

Further, manganese is sometimes present. In this case, the tin, lea copper are determined by the methods given for complex brasses. Th and manganese are then precipitated with hydrogen peroxide and amn the filtrate being employed for the determination of the nickel and z already described. The iron and manganese precipitated with hydrogen pe and ammonia may be separated and determined electrolytically or volumet (*see* Complex Brasses); or the ferric and manganese oxides may be w together, then dissolved in hydrochloric acid, and the iron separated as acetate.

⁂

As is seen from the following table (Lunge), alloys of copper, nickel an vary in composition according to their origin, purpose, etc.

TABLE XXXV

**Compositions of Argentans**

| | Cu | Ni + Co | Zn | Mn | Fe |
|---|---|---|---|---|---|

eces. The alloy is analysed like argentan. Usually, however, determine only the layer of silver and this may be effected as

**nation of the Silver.**—1. After being well cleaned and freed the object is suspended by a platinum wire in a 2–3% potassium ion in a tall, narrow cylinder and is connected with the positive rrent source. A thin, clean copper sheet in communication ative pole, is also suspended in the liquid but not in contact ect. The current (0·1–0·2 ampere) dissolves the silver from nd deposits it on the copper. When the de-silvering is comhe object and the silvered copper are removed and washed, ing dissolved in nitric acid, the solution diluted and the silver by a slight excess of hydrochloric acid ; the silver chloride is a Gooch crucible, washed, dried and weighed.

rocyanic solution is acidified with dilute hydrochloric acid *l*), the liquid evaporated until cyanogen compounds are comnated, and the precipitated silver chloride weighed. From ne two quantities of silver chloride the amount of silver on the culated.

ticle, or part of it, is freed from grease, weighed, and gently a mixture of 9 vols. of conc. sulphuric acid and 1 vol. of conc. By this means all the surface silver is rapidly dissolved, whilst neath is not at all or but little attacked. When the de-silvering the object is withdrawn, washed rapidly and thoroughly with l and weighed. The loss in weight gives the silver plating.

ore rigorous determination the silver dissolved may be estiluting with water the nitric-sulphuric solution, together with water, and determining the silver either volumetrically by ethod or gravimetrically as chloride.

## ALUMINIUM AND ITS ALLOYS

its lightness and stability, aluminium is now used for making e objects in common use and for naval and flying construction. minium forms a constituent of numerous alloys, many of which cally superior to pure aluminium. Among these are : *Light ronze* (Al with 3–8% Cu) ; *Magnalium* (Al with 3–15% Mg) ; *lloy* (Al with 10% Sn) ; *Ziskon* (Al with varying proportions *luminium-nickel* (Al with 1–3% Ni) ; *aluminium-manganese*

n washing is effected by taking the ob'ect quickly from the acid mixture

0·5% Mg) ; *Zisium* (Al with varying quantities of Cu, Sn, Zn) ; *Al*
(Al with 10–20% Sn, 4–6% Cu). There are also many other all
aluminium, nickel and iron ; aluminium, copper, lead, nickel and iro

For commercial aluminium and its more important light alloys, a g
method of analysis will be indicated, whilst for light aluminium-bron
for magnalium, which could also be analysed by the general method, s
and quicker methods are given.

For aluminium-copper alloys in which the copper predominates (
aluminium-bronzes, aluminium-brasses, etc.), reference should be
to copper and its alloys and for iron-aluminium alloys (ferro-alumi
to ferro-metallic alloys.

## ALUMINIUM

The elements usually present as impurities in commercial alum
are copper, lead, iron, zinc, carbon, silicon and sodium. To form t
called *light alloys*, the aluminium may be associated with tin, copper
nickel, cobalt, manganese, lead, magnesium, etc.

Thus, the analysis of commercial aluminium or of its lighter
includes [1] :

**1. Determination of the Copper, Lead, Iron, Zinc, Mang
and Cobalt.**—*A*. In absence of Nickel. From 2 to 4 grams of the s
—according as the extraneous metals are present in larger or smalle
portion—in minute fragments are treated in a flask (about ½-litre)
five times their weight of tartaric acid and a little water. The fl
covered with a small funnel and a small quantity of hydrochlori
diluted with an equal volume of water added drop by drop. The ac
started by gentle heating and sometimes proceeds so vigorously as to r
cooling. When the evolution of hydrogen begins to slacken, a fresh qu
of hydrochloric acid of the same concentration is added and the
heated on the water-bath until the action is complete, care being ta
use the least possible amount of acid. The heating is then continu
some time, with addition of 2–3 c.c. of conc. nitric acid.

The solution, which is usually turbid owing to the presence of c
and silica, is treated with small quantities of 50% sodium hydroxide so
until the voluminous aluminium hydroxide precipitate at first f
redissolves in the excess of the reagent. Hydrogen sulphide is then p
through until the supernatant liquid becomes faintly yellow and the so
boiled for some minutes to facilitate separation of the sulphides, le
a time on the water-bath and filtered into a 300 or 500 c.c. measuring
the precipitate being washed with ho water containing a few d

by heating on a water-bath and the clear liquid treated with dimethylglyoxime solution in slight excess. After a short ater-bath the precipitate is collected in a Gooch crucible, washed hot water containing a little ammonia and ammonium tartrate th hot water alone until the filtrate is neutral, dried at 120° : nickeloxime × 0·2032 = nickel.

te is heated on a water-bath to expel the alcohol and then just sufficient hydrogen sulphide to precipitate the metals in subsequent procedure being as in *A* (above).

**mination of the Tin.**—The sodium or ammonium sulphide he 300 or 500 c.c. flask is made up to volume and an aliquot 150 c.c.) treated, in a ½-litre flask covered with a small funnel, antities of hydrochloric acid and with shaking until the re- d. A further quantity of 25–30 c.c. of conc. hydrochloric acid the liquid boiled, if necessary with addition of a few crystals chlorate, until the tin sulphide at first separating redissolves s of hydrochloric acid.

ion is then treated with 25–30 grams of ammonium oxalate sed at 50–60° to determine the tin (*see* Electrolytic Determina- in Ordinary Bronzes).

**mination of the Carbon.**—This is carried out directly on a le sample by either the Corleis method or the copper chloride Determination of Total Carbon in Iron).

**mination of the Silicon.**[2]—1 gram of the aluminium in nts is dissolved in 300 c.c. of a mixture of 100 c.c. of nitric ), 300 c.c. of hydrochloric acid (D 1·2) and 600 c.c. of 25% d. When the action comes to an end, the liquid is heated a sand-bath until abundant white sulphuric acid fumes appear. le residue is taken up with water acidified with sulphuric acid, ssolve the aluminium sulphate and filtered, the vessel and filter l first with water acidified with sulphuric acid and then with The residue on the filter, consisting of silica, graphitic silicon lumina, is dried, ignited and fused with sodium carbonate, the eing dissolved in water acidified with hydrochloric acid and o dryness ; this treatment with hydrochloric acid is repeated s and the residue finally heated in an oven at 135° to render mpletely insoluble (*see* Iron, 2).

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t present is determined electrolytically under the conditions indicated nination of the nickel.

g to I. O. Handy: *Journ. Amer. Chem. Soc.*, *XVIII*, p. 736.

ce of lead, the washing is carried out first with hydrochloric acid (D 1·2) in a platinum crucible and weighed; it is then evaporated on a water-bath with a few drops of sulphuric acid and a few c.c. of hydrofluoric acid, heated to redness and weighed. The loss in weight gives the silica: $SiO_2 \times 0{\cdot}4693 = Si$.

**5. Determination of the Sulphur, Arsenic and Phosphorus.**—10 grams of the sample are introduced into a flask fitted with a tapped funnel and a gas-delivery tube connected with absorption bulbs containing bromine water, and very dilute hydrochloric acid slowly run in through the funnel until the metal is completely attacked. The sulphur, phosphorus and arsenic are oxidised by and retained by the bromine water, one-half of which is used for the determination of the sulphuric acid by precipitation with barium chloride. The second half is freed from the excess of bromine and the arsenic precipitated by means of hydrogen sulphide and determined as usual. The filtrate from the arsenic precipitate is freed from excess of hydrogen sulphide and the phosphoric acid then precipitated with ammonium molybdate (*see* Determination of the Phosphorus in Iron).

**6. Determination of the Sodium.**[1]—5 grams of the sample are heated gently with nitric acid (D 1·15), the solution evaporated in a porcelain dish, the residue dried and heated for a long time on a sand-bath, but without melting the sodium nitrate formed. When cold the residue is taken up in boiling water, the solution filtered and the filter washed with boiling water, the filtrate being evaporated to dryness repeatedly with hydrochloric acid to expel the nitric acid and the residue heated to about 300°, allowed to cool, dissolved in water and the chlorine estimated; the corresponding amount of sodium is then calculated.

Lunge [2] observes that a little sodium aluminate is formed under these conditions and advises the treatment of the aqueous solution with ammonium carbonate to precipitate the aluminium and the determination of the sodium as sulphate in the filtrate.

**7. Determination of the Aluminium.**—0·6 gram of the sample, reduced to fine fragments, is treated in a flask covered with a small funnel, with hydrochloric acid diluted with an equal volume of water. When the action is complete, the solution is evaporated in a platinum dish on a water-bath, this evaporation with dilute hydrochloric acid being repeated several times and the residue finally heated in an oven at 135° to render the silica insoluble. The latter is treated with hot water acidified with hydrochloric acid and filtered into a 250 c.c. beaker, in which it is subjected to a current of hydrogen sulphide. The precipitate is filtered off and both vessel and filter washed with hot water containing hydrogen sulphide, the d ferric hydroxides filtered off, washed, dried and weighed in y manner. This amount, less that of the ferric oxide previously s the alumina and hence the aluminium.

ron has not been determined previously, it may be estimated of aluminium by means of cupferron.

purpose, 100 c.c. of the liquid in the flask are treated in a 250 with constant shaking, with 6% aqueous cupferron (ammonium osophenylhydroxylamine) until the precipitation of the iron is ·1 gram Fe requires 0·833 gram of the reagent). The end of the etected by pouring a little of the reagent down the side of the en iron is still present, a reddish-brown precipitate is formed absence of iron a white, crystalline precipitate is formed owing t solubility of the reagent in an acid medium.

e precipitation of the iron, the liquid is left for 15–20 minutes ltered, the precipitate being thoroughly washed first with 2N c acid, then with slightly ammoniacal water to eliminate all e reagent, and finally with distilled water. The moist filter tate are then carefully ignited in a porcelain crucible, the weight ferric oxide.[1]

**ermination of the Nitrogen.**—From 3 to 4 grams of the sample ed, in a flask fitted with a tapped funnel and a gas delivery tube, sodium hydroxide solution, the gas generated being collected in ochloric acid. At the end of the action, the flask is boiled for 5 minutes to displace all the ammonia and the nitrogen in the ic acid then determined colorimetrically with Nessler solution, being made with a standard ammonium chloride solution.

⁂

m of good quality should be white with only a faint blue tint and ighly ductile and malleable, while its fracture should be finely crys- orm, and free from sponginess or slag. Its specific gravity should be and 2·7 (the value increases with the degree of impurity) and the of aluminium at least 97–98, the total amount of elements commonly ing the aluminium (silicon, iron, copper) not exceeding 1·5–2%. to Moissan, a particularly harmful influence on the strength and of the aluminium, especially when this is to come into contact with xercised by sodium, which may be present in the proportion of 0·1– ssan) or, according to some, in even larger amounts (up to 4%). o Foundry, aluminium also contains 0·04–0·12% of nitrogen. The s of various samples are given in the following table (Moissan, , Lunge) :

be executed in duplicate.

**1. Determination of the Silver.**—The methods most commonly used are: the dry or cupellation method, Volhard's volumetric method with thiocyanate, and Gay-Lussac's sodium chloride method.

(*a*) CUPELLATION METHOD. This method is based on the fact that the noble metals, silver, gold and platinum, are unoxidisable at the highest temperatures, whilst copper and other metals usually alloyed to the precious metals oxidise easily and, if in presence of a certain quantity of lead—which gives a readily fusible oxide—penetrate by imbibition into the cupel. Thus, the noble metals are separated in the form of a drop, which, on cooling, yields a button capable of direct weighing.

*Apparatus and reagents.* (1) Muffle furnace, either coal or gas, the latter more easy to manipulate and regulate. In order to protect the operator from the intense heat of the furnace, the latter is usually placed in an adjacent room close to the dividing wall, a small aperture in which gives access to the orifice of the muffle.

2. Cupels. These are capsules having the form of an inverted, truncated cone and made with bone dust carefully powdered, calcined, washed and pressed in a mould. A good cupel should absorb its own weight of lead.

3. A thermo-electric couple with the corresponding pyrometer voltmeter, to measure the temperature of the muffle. The couple is placed in the muffle so that its extremity is very close to the cupel.

4. Lead free from silver. That obtained by reducing litharge could be used but its price is too high. Lead almost entirely free from silver is, however, sold and is quite suitable; 20 grams of it should be cupelled as a check.

*Preliminary test.* The amount of lead to be used for the cupellation varies with the silver content of the sample, so that it is necessary to make a preliminary test. The external characters and a test on the touchstone are sufficient to a skilled operator. A beginner may make use of a method which is sometimes employed and which consists in cupelling 0·1 gram of the sample with 0·5 gram of lead if the metal is soft and white, with 1 gram of lead if it is hard, or with 1·5 gram, if it appears reddish.

The amounts of lead to be used for different degrees of fineness are as follows:

| Degree of fineness of the alloy. | Amount of lead to cupel 1 gram of the sample |
|---|---|
| 1,000 | 0·3 gram. |
| 950 | 3·0 ,, |
| 900 | 7·0 |

, the weight of which is allowed for in calculating the amount used, and placed on a tray consisting of a sheet of copper pro- handle and stamped into cavities to take the test pieces. Be- tton is placed the necessary quantity of lead.

s are placed in the muffle and close to them the thermo-electric temperature being then raised to bright redness, that is, to When these have assumed the temperature of the muffle the absence of a dark zone between the bottom of the cupel of the muffle), the pieces of lead are introduced into the cupels suitable tongs. The lead at first melts and becomes covered of oxide and after some time *uncovers*, that is, assumes a shiny

lead is uncovered, the test pieces are placed in the cupels with avoid loss by projection, the door of the muffle being left open ermit of observation and to give access to the air. The test nd a shining appearance is resumed. Over the surface of the which is at first only slightly convex, luminous points are seen ecome absorbed by the cupel. As the cupellation proceeds the creases and the drops of fused litharge, of oily appearance, r and circulate more rapidly. At this point the temperature sed a little by closing the door of the muffle and increasing the he furnace, in order to oxidise the last particles of lead and ton of silver fused. As the last portions of lead "pass" from e molten metal, which is in a state of considerable agitation, nd of iridescence, this soon disappearing; the button then ue and still, but suddenly flashes out brightly. This indicates ne operation.

s are then gradually brought near to the door of the muffle ttons of silver may cool slowly and rapid release of the occluded d silver absorbs up to 22 volumes of oxygen) not give rise to *bitting or vegetating*) of the metal. After a few minutes the thdrawn from the muffle and the metallic buttons detached, ghtly on both sides, held in tongs and freed with a scratch- e adherent cupel dust and weighed.

weight of the two test pieces in milligrams, if these were each r this weight divided by two, if the samples were 1 gram each, eness of the alloy.

pellation is successful, the silver buttons obtained from the

---

ples of silver and gold, to obtain the highest accuracy and to be able y, very sensitive balances are employed with an exactly equally divided with very small movable dish-shaped pans, on which the test pieces white lower ones, and should differ in weight by a few milligrams at

The method of cupellation, largely used for the analysis of argentif minerals and for the control of intermediate products in the extraction of s as well as for the by-products and for low-grade alloys, is not advisab analysing ordinary jewellery, coinage, etc., since, however carefully it is ca out, the results obtained are not always concordant and never very exact, mostly somewhat low. The errors are due principally to volatilisation c silver and absorption by the cupel. Tables showing the corrections to be ap have been prepared, but the best method of determining such correcti to carry out a *check* determination, at the same time and under the same ditions, with pure silver and pure copper in approximately the same propo as in the sample.

As regards the influence of extraneous metals on the results, it shou borne in mind that gold and platinum *remain with the silver and increase its w* They may be detected by treating the button with nitric acid and examinin black powder remaining undissolved. In low proportions, arsenic, tin, antin bismuth, iron, nickel and cobalt do not interfere appreciably with the oper

(*b*) VOLHARD'S METHOD.[1] This method consists in precipitatin silver in nitric acid solution with standard ammonium thiocyanate sol in presence of ferric sulphate as indicator. As soon as the precipitati the silver is complete, the thiocyanate reacts with the ferric salt and a persistent red coloration, which marks the end of the reaction.

*Reagents.* (1) A solution containing 3·1–3·2 grams of ammo thiocyanate, free from chlorides, per litre.

(2) Cold saturated ferric ammonium alum solution free from chlo and treated with a little nitric acid to destroy the brown colour; the amount (2–3 c.c.) is used in each titration.

(3) Pure silver (*fine silver*). This may be obtained in foil from repu firms.

Where many tests are made the fine silver is prepared in the labor from the silver chloride residues from Gay-Lussac's method or from chloride precipitated from the silver nitrate solutions obtained in the *q tion* of gold (*see* later). Failing these, commercial silver of 999 finen dissolved in nitric acid, allowed to stand for some days in the dark, fi to remove traces of undissolved gold and the silver precipitated w slight excess of dilute hydrochloric acid.

In whatever way obtained, the silver chloride is washed free from dissolved in ammonia, left for some days and then filtered, the clear so being made acid with dilute hydrochloric acid to precipitate the chloride, which is again washed free from acidity and redissolved in amm After standing for some time, the solution is filtered, treated with s hydroxide in the proportion of 750 grams per 1000 gram f the c

with 5–10 c.c. of nitric acid (D 1·2) in a conical flask covered
ntil the metal is dissolved and the red fumes have disappeared. removed after *cooling* and washed with distilled water, the treated with 50 c.c. of cold water and 2–3 c.c. of the ferric and the thiocyanate solution gradually run in from a burette liquid assumes a persistent pink tint. It is usual to adjust of the thiocyanate solution so that 0·2 gram of silver requires c.

*in the actual test.* Exactly 0·2 gram of the sample is dissolved [2] as described above and the solution diluted and titrated cyanate.

rd method is very rapid and applicable to alloys of any degree is not so exact as Gay-Lussac's method (*c*). Further, it cannot ence of mercury or palladium, since these metals also react with Also, with more than 70% of copper, the blue coloration renders less exact; in this case fine silver may be added so as to diminish of copper. Nickel and cobalt have a similar effect to copper.

USSAC'S METHOD. This was proposed in 1832, when the ter of Finance appointed a commission, of which Gay-Lussac er and also reporter, to study the causes of error in the determination silver by the cupellation method.[3]

s in adding to a nitric acid solution of the sample sufficient de solution to precipitate almost the whole of the silver, and the small amount of silver remaining in solution from the y produced by addition of a fresh quantity of the sodium ion. With a little practice, 1 part in 10,000 may be determined tely by this method. Since it requires a knowledge of the composition of the sample, a preliminary test by Volhard's y cupellation is necessary.

s. 1. Ordinary bottles of about 200 c.c. capacity, fitted with ground stoppers and with a distinctive mark on both bottle

.c. pipette. The pipettes used by assayers are usually without o facilitate reading, are fixed in a stand (Fig. 24).

accuracy of measurement is, however, obtained by means of tte (Fig. 25), which is a 100 c.c. pipette drawn out to a point

hod for obtaining fine silver is that adopted by the testing laboratory talian Mint at Rome.

us fumes should be present in the nitric acid used and those formed ction should be completely expelled, since nitrous fumes—and nitric he hot—decompose thiocyanates.

ac: *Instruction sur l'essai des matières d'argent par la voie humide*, Paris,

glass basin to catch the overflow, while the lower end is connecte
rubber tube and tap with the vessel containing the sodium chloride s
fixed at a convenient height. The pipette is filled by opening the ta
allowing the liquid to flow gently over. When the liquid begins to ov
at the top, the latter is closed by means of the index finger of the left
while the tap is shut and the rubber tube carefully detached with t
hand. The lower end is then touched outside with a dry vessel to r
the small amount of adherent liquid and the bottle placed centrally

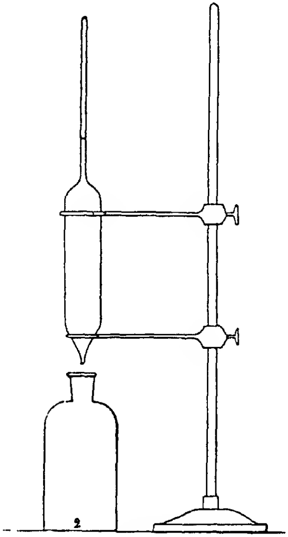

FIG. 24

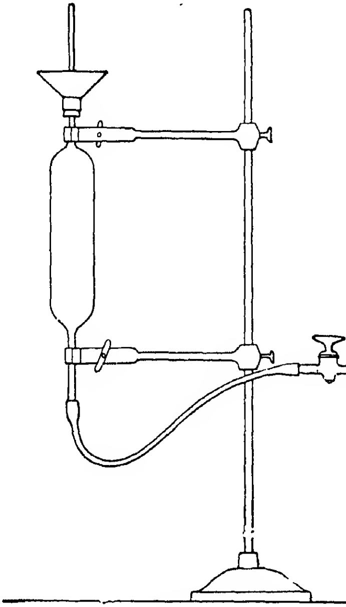

FIG. 25

the pipette. The finger is then withdrawn from the top and all the
flowing in a continuous jet, but not the drops falling subsequently, a
to run into the bottle.

The pipettes should be kept perfectly free from grease and, befor
should be washed at least twice with the solution to be measured.

3. A shaking apparatus, which may be one of those commonly em
in chemical laboratories for bottles. In assayers' laboratories special
forms of apparatus are used to protect the bottles from the action
light. They take 10 bottles at a time and are often, as in the Mint at
worked electrically. The shaking should be rapid and vigorous.

4. A kind of tray with cells for carrying 10 bottles, screened fro

becomes directly illuminated it is easy to discern the cloud new addition of solution.

. *Standard salt solution,* 100 c.c. of which precipitates almost ram of pure silver. It is prepared by dissolving 5·4200 odium chloride to 1 litre with distilled water or 5·570 grams d between filter papers, to 1 litre with ordinary water [1] and, ise, filtering the solution.

*ndard salt solution,* one-tenth as strong as the preceding vhich it may be prepared by dilution; or 0·5420 gram of loride may be dissolved to 1 litre. This solution, 1 c.c. of ds with 0·001 gram Ag, is stored in a bottle fitted with a traversed by a pipette graduated from 1 to 5 c.c.

ic acid, D 1·2, free from chlorine.

*on of the salt solution.* 1 gram of pure silver (fine silver, ethod) is weighed with the greatest accuracy [2] and heated in one of the test bottles with 8–10 c.c. of nitric acid (D 1·2) is dissolved and the red vapours have disappeared. After of the bottle is washed with a few drops of water and 100 lard salt solution introduced by means of one of the pipettes being taken that only the liquid falling in a continuous nd not the subsequent drops. The bottle is then stoppered about 10 minutes in the shaking apparatus, the precipitate ie liquid becoming quite clear. With a rapid shake the cipitate are removed from the upper part of the bottle, the en placed on the bench, the stopper removed and 1 c.c. of dard salt allowed to flow gently down the side of the bottle. es the bottle is raised so that the upper portion of the liquid iated, fresh precipitation of the silver in the form of a cloud of the liquid being usually observed.

1 is exact when this cloud is barely perceptible and when gently shaking the liquid; if there is too much cloud, the on must be corrected by addition of salt, whilst, if no cloud e solution must be diluted. Only the first case will be con- second may be reduced by suitable dilution to the first. on of 1 c.c. of the weaker standard salt produces too intense ottle is shaken in the apparatus for 10 minutes and, after d with a further 1 c.c. of the weaker salt. This process is such an addition causes either no further precipitation or perceptible cloud. In calculating the correction, the last glected or taken as only 0·5 c.c. in the first case, but must account in the second case. If, for instance, the complete

plus 3 c.c. of the weaker standard salt solution, to every 100 c.c standard salt it will be necessary to add a quantity of sodium corresponding with that contained in 3 c.c. of the weaker standa (0·000542 × 3) gram if pure salt has been used, or (0·000557 × with sea-salt. After this new quantity of salt has been added and di the resulting solution is tested to ascertain if any small correctio necessary.

The temperature of the standard solution, corrected in this noted. Each time it is used, it should be well shaken to render i geneous.

*Actual test.* We will suppose that the preliminary test of an silver and copper by Volhard's method gives the approximate finen A weight, 1·201 gram, is taken, this containing very slightly more gram of silver. Two pieces, each of this weight, are placed in tw bottles and treated with 8–10 c.c. of nitric acid (D 1·2) with the pre mentioned above. When cold, 100 c.c. of the standard salt sol run into each bottle, which is then shaken, the further procedu as described for the standardisation of the salt solution. If, in to the 100 c.c. of the standard salt solution, 1 c.c. of the weaker s is required, the amount of the silver in the 1·201 gram of the sam be 1·001 gram, the fineness of the alloy being 833·4 (1201 : 1001 833·4).

To obtain greater accuracy, the weaker standard salt solution added in portions of 0·2 c.c. A practised observer, however, by co the intensity of the cloud given by the check with that given by the can estimate accurately by the eye 0·1 c.c. of the weaker stand solution. In special works dealing with this subject, tables com Gay-Lussac are given which render unnecessary the calculation happens that the addition of 1 c.c. of the weaker standard salt no cloud, it is best to repeat the test with a larger quantity of the

Gay-Lussac's method, although expeditious, is undoubtedly the m of all and is universally employed for the control of silver coinage. the accuracy of the results depends on the accuracy of the weighing ticularly on the accuracy with which the standard solution is measure = 0·5 milligram Ag). It is necessary also to allow for variations of tem since at different temperatures the amount of sodium chloride cont 100 c.c. of the standard solution varies appreciably (1° higher or lo introduce an error of about 0·2 in the fineness). To eliminate this error, Gay-Lussac tried weighing the standard solution instead of m it, but found this procedure so much less expeditious that he discarde compiled a table giving corrections for temperature. In practice the means of avoiding such an error is to carry out, at the same time as

s used in the Brussels mint, is rather more delicate than that
out it requires perfect expulsion of the nitrous vapours and
ns to prevent access of light to the tests, etc.
the Gay-Lussac method is carried out as described above, the
lver nitrate being suppressed and identical conditions employed
est and that on the sample, all causes of error are eliminated.
e influence of extraneous metals, it must be borne in mind that
he accuracy of the results, as it also is precipitated as mercurous
his metal is present, it is expelled by heating the alloy to fusion
cible. When tin, antimony or bismuth is present, an opalescent
l in which it is difficult to observe the formation of cloudiness.
timony or bismuth a little tartaric acid (1–2 grams) is added,
alloy contains tin or a large proportion of lead, it is advisable
ulphuric acid. Further, gold in proportion exceeding a fineness
influences the results as it withholds a little silver. Copper in
than 50% gives coloured solutions, which render observation

**nation of the Gold.**—In a flask with a long, narrow neck,
sample are dissolved in 80–100 c.c. of nitric acid (D 1·2),
ng decanted off and the residue again boiled with nitric
lso decanted. The residue is washed repeatedly with hot
ation and the undissolved gold remaining as a black powder
ractory, unglazed crucible (*see* Gold and its Alloys—Quarta-
ited and weighed.

**n of Tin, Antimony, Copper, Bismuth and Lead.**—
sample are treated with nitric acid (D 1·2). In presence
ny, the liquid is opalescent or contains a slight white pre-
filtered solution is rendered alkaline with ammonia, it
r less intensely blue if copper is present, whilst a flocculent
orm in presence of bismuth or lead, which may be identified
eans.

⁂

rude silver often contains small quantities of gold, lead, mercury,
, arsenic and sometimes selenium and bismuth. The presence
remely harmful, alloys made with silver containing only traces
rough and brittle. Refined silver is usually very pure, the
ntaining, on the average, 99·9% Ag.
especially alloyed with copper for jewellery, coinage, etc. The
Italian 5-lire pieces is 900 fine with a variation of 2 either way,
is usually 900 fine, and that for jewellery 800 or even less—
.

The more important commercial products are : gold in bar granules, powder, etc., and its alloys with copper alone and with sil copper.

## GOLD

The essential determination to be carried out on the metal is the gold, the fineness being the amount of gold per 1000 parts of th This determination is made as in alloys of gold and copper (*q.v.*).

## ALLOYS OF GOLD AND COPPER

The most important determination is :

**1. Determination of the Gold.**—By cupellation in presence the gold is separated from copper and other ordinary metals wit it may be alloyed, but not from silver, which resembles gold in b oxidisable at the highest temperatures. To eliminate the silver always accompanies gold in larger or smaller proportion, it is nece treat with acid. Experience has shown that, for the complete eli of the silver, the latter must be in considerable excess, namely, parts to 1 part of gold. It is, therefore, necessary, *before cupel* add silver to make this relation hold. The assay of gold hence c two distinct operations :

(1) Cupellation in presence of lead and silver to eliminate metals and to form the alloy of gold and silver in the above pro an operation termed *inquartation*, since the gold constitutes ab fourth of the resulting alloy.

(2) Treatment of the latter with acid to remove the silver, this being known as *parting*.

To calculate the quantities of silver and lead to be used in the cu the gold content of the sample must be known approximately. It sary, therefore, to make a preliminary assay and this is usually means of the touchstone.

Preliminary Touchstone Assay. This consists in tracing with the sample on the touchstone beside streaks traced with gol alloys of known fineness and comparing the colours of the streaks b after treatment with acid.

This test requires :

(1) *The touchstone.* A good stone should be unattackable by should be of a uniform black colour, hard, of fine grain and opaque

etween 350 and 500, the 750 acid for finesses 500–750, and finenesses above 750. The compositions of these acids are :

| . | 750 acid. | 900 acid. |
|---|---|---|
| ·384), 40 | Nitric acid (D 1·346), 98 c.c. | Nitric acid (D 1·384), 40 c.c. |
| acid (D | Hydrochloric acid (D 1·171), 2 c.c. | Hydrochloric acid (D 1·19), 5 c.c. |
| 20 c.c. | Distilled water, 25 c.c. | Distilled water, 15 c.c. |

*e* consists in rubbing the sample on the stone so as to leave -4 mm. wide and 15–20 mm. long, and quite close to this, h two needles one less and the other more fine than the cters of the alloy would indicate for it. The streaks are e light and compared. A little of the acid corresponding ess of the comparison needles is then rubbed with a glass reaks, which are then compared, dried with absorbent paper, vith acid, again dried, and the residues of gold on the stone om the colour of the streaks before treatment with acid cy of those remaining after the action of the acid, the approxi- of the alloy is judged. If the streak left by the sample is e with those of the needles, the test must be repeated with ner or lower fineness.

ST. *Apparatus and reagents.* (1) A muffle furnace, cupels, lectric couple like that used in the cupellation of silver (*q.v.*). f 999 fineness absolutely free from gold, and lead which need m silver.

resistant pear-shaped flasks with stout, very long necks (assay rucible of very fine refractory earth or of unglazed porcelain

*silver and lead to be used in the cupellation.* The assay of ed out in duplicate on 0·5 gram of the sample, and the amount added for the inquartation is about three times (more exactly t of the gold. Thus, if the touchstone assay indicates an neness of 900, the amount of silver to be added to each 0·5 lloy is 0·9 × 2·5 × 0·5 = 1·125 gram. The silver, which is nearest centigram, should be in sheet which is not too thin, ece used in each case forms two squares of 0·5 cm. side.

t of lead required is also related to the fineness of the alloy by the following table :

| ss of<br>nple. | Amount of lead (grams) required per 0·5 gram of sample. |
|---|---|

of about 0·5 cm. side. This is placed between the two pieces of silv and the whole wrapped in a piece of white paper or of thin lead foil (all for the weight in calculating the lead to be taken) and placed in th beside the corresponding quantity of lead.

Meanwhile the furnace is started and the cupels, from which th has been blown, introduced. In gold assay there is no danger of se loss owing to volatilisation, so that a rather higher temperature th silver may be used. According to T. K. Rose,[1] the most suitable mear perature is about 1070°, each 5° above this causing a loss of 0·01 on th ness. When the temperature indicated is reached, each cupel is cl with the weighed quantity of lead, which rapidly melts, becomes co with a layer of oxide and, after a few instants, becomes uncoverec shining. With great care, to avoid spurting, the little parcel of s and silver is placed in the cupel. The phenomena of the cupellatic identical with those observed with silver ; after some time the agi

Fig. 26

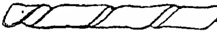

Fig. 27

on the surface is observed, then the iridescence, and finally the bright fla The cupels are then moved towards the door of the muffle, allowed t somewhat and withdrawn, the buttons being detached with a su utensil. With successful cupellation, the buttons should be hemisph shining and white at the upper part and opaque white at the lower. button is held in strong pincers, the edges struck with a hammer ar flat part freed from cupel dust by means of a stiff brush. It is then on a clean anvil and struck alternately on the sides and on the flat p as to give it a somewhat elongated form and is next reheated to redn leaving it for a short time on a cupel in the front part of the muffle. cool, it is rolled to obtain a strip (*fillet*) about 0·5 mm. thick and of the shown in Fig. 26. This strip, bent in two in a smooth curve, is again rel to redness for 4-5 minutes on a cupel. When cold, it is twistec a spiral round a glass rod so as to obtain almost a tube about 0·5 cm (*cornet*), care being taken that the rolls of the spiral do not touch (Fig this is then subjected to the operation of parting.

*Parting.* Each of two assay flasks is charged with 25–30 c.c. of acid (D 1·2) absolutely free from chlorine, nitrous fumes and selenic this being heated to boiling and the two cornets introduced. The h is continued so as to maintain the liquid in gentle ebullition for ten m after volution of nitrous vapours ceases.[2] After a sho

e. The residue is again boiled for 10 minutes with 20 c.c. ) 1·3). With the more concentrated acid the boiling is less gerous bumping may occur, and some authorities recommend a scrap of wood charcoal or a completely charred pepper- is second portion of acid has been decanted off, a further :.c. of nitric acid (D 1·3) is added and boiled for 10 minutes ast traces of silver. When this last acid together with the al have been removed, the cornet is washed with two quan- c.c. of boiling water, the flask being subsequently filled 1 cold distilled water. The mouth of the flask is then closed inverted crucible of refractory earth or unglazed porcelain, firmly on while the flask is inverted. A little water descends le and forms a hydraulic seal, while the brittle and slender alls to the bottom of the crucible. After some time, when ments detached from the cornet have been deposited, the y raised to the edges of the crucible, displaced a little laterally id movement brought into an erect position. The water is the crucible which is dried on the platform of the furnace :ly heated to redness in the muffle for 2–3 minutes. Under the heat the cornet contracts to about one-third of its original ,umes a golden-yellow metallic appearance. When cold, the e weighed together, the total weight giving directly the sample; the weights of the separate cornets should not than 0·5 milligram.

.y of gold by cupellation, small losses occur (according to the fineness) owing partly to volatilisation of the gold and ɔition by the cupel. This slight loss is, however, compen- all amount of silver (0·75–1 one-thousandth) which always he gold in spite of the different treatments with nitric acid. g to Rose, if the operation is properly conducted, the error eed ± 0·2 per thousand. The losses by volatilisation increase .nt of lead used and, consequently, with diminution of the old in the alloy; on this account, Riche advises the omission eatment with nitric acid in the case of gold-copper alloys of than 800. In some laboratories the small errors are esti- .ng a control assay with pure gold [1] and pure copper in about ortions as in the sample, the mixture being cupelled with tities of silver and lead, and the parting carried out under itions. In assaying commercial fine gold Riche advises the per thousand of copper to prevent brittleness in the button of twice as much lead as is indicated in the table ; after the partin cornets are weighed, again subjected to inquartation with silver a per 1000 of copper and again parted with acid of D 1·3, these oper being repeated until the cornets are of constant weight.

Palladium has no injurious effect, since it dissolves completely in acid.

Iridium causes the formation of black spots on the button, these re ing even after parting. If the gold is dissolved in aqua regia, the ir remains undissolved and may be collected and weighed.

## ALLOYS OF GOLD, SILVER AND COPPER

In the assay of these alloys, three cases are distinguished :

(1) Rich alloys, in which the proportion of gold to silver is highe 1 : 3.

(2) Medium alloys, with a proportion of about 1 : 3.

(3) Poor alloys, with a proportion less than 1 : 3. The assay of alloys includes two operations :

(1) Cupellation, which gives the gold and silver together.

(2) Parting, which gives the gold alone.

Preliminary test. In presence of silver the touchstone assay do always give reliable results (the presence of silver is easily detected formation of a slight, white precipitate on the streak when treatec the acid), so that a preliminary assay by cupellation is advisable. made with 0·250 gram of the sample and 4–8 grams of lead, accord the supposed richness in copper, the button of gold and silver being wei the weight of the sample, less that of the button, gives approximatel of the copper. The button is then rolled, the strip treated with nitri and the remaining gold weighed ; the proportion of silver is then fou difference.

I. Rich Alloys. (*a*) *Determination of the gold.* This is carried two separate portions of 0·5 gram under the conditions given for the mination of gold in gold-copper alloys. The inquartation silver m diminished in amount by the approximate silver content indicated preliminary assay (*see* p. 287). The amount of lead required is bas the total fineness and on the ratio between the gold and silver (*see Medium Alloys*).

(*b*) *Determination of the silver.* 0·5 gram of the alloy is cupellec the quantity of lead used for the determination of the gold, the res button representing gold and silver together ; the latter is thus fou difference.

tion of gold and three fourths of that given for the silver, being taken.

If the preliminary assay gives Au 220 and Ag 680 per 1000, ness is 900. For this value the table for the cupellation of dicate 5 grams of lead, so that 1·25 is taken, and the table ation of silver would indicate 3·5 grams of lead, so that 2·6 ) is taken; the total amount of lead taken is thus 1·25 + ams.

ns obtained are weighed together and subjected to parting. ven by the total weight of the two cornets and the silver by tton minus gold).

ALLOYS. Two 0·5 gram samples are cupelled as described ation of silver and with the amounts of lead there prescribed; ire is, however, kept somewhat higher, especially if the fineness xceeds 50 per thousand. The sum of the weights of the two the silver + gold. To separate the silver, the buttons are ng in mind that, if the fineness of the gold is not more than ie two buttons should be parted in the same flask, and that, eeding 20 per 1000, the buttons should be rolled and reheated ss; further, that, before decanting the acid from the flask, ould be given a rotary motion, so that the gold dust collects ; that the third treatment with acid should be omitted and re is necessary to avoid loss during the descent of the gold crucible.

content does not exceed 60–80 per 1000, the silver may be vith greater exactitude by the Gay-Lussac method (*see* Silver ys).

⁂

contains considerable quantities of impurities, especially silver, bismuth, tin, antimony, arsenic, etc. Thus, gold obtained by varies from 865 to 970 fine, whereas that given by the Siemens fineness of 890–900 and contains, besides silver, only traces of ad; gold precipitated by zinc is 600–700 fine and contains con- portions of zinc, lead, iron and copper.

*d* reaches the fineness 993–999, but always contains small quan- .

sed more especially alloyed with copper for jewellery, coinage, The *legal fineness* of the *Italian gold coinage* is 900 ± 1 and that nage 916·66. With jewellery, plate, etc., the fineness may vary 500.

and gold-silver-copper alloys are also largely used, more especially cial effects in articles of jewellery (green gold: 750 Au, 250 Ag;

## GOLD-PLATING

## (Gilding)

**1. Technical Test.**—The surface of the object is rubbed repeatedly with a small piece of very fine glass paper (No. 000) so as to concentrate any gilding at one point of the glass paper. This point is then treated with a drop of conc. nitric and one or two drops of conc. hydrochloric acid and warmed gently over a very small flame until the metal is dissolved. The solution is then washed into a test-tube with 1–2 c.c. of water, the liquid being filtered if turbid and heated with either an equal volume of fresh sulphur dioxide solution or a few drops of fresh stannous chloride solution. In presence of gold, a violet red, varying coloration is observed owing to the formation of purple of Cassius

**2. Test for Small Objects.**—The sample, or part of it, or a number of small pieces, according to circumstances, are heated on the water-bath with nitric acid diluted with an equal volume of water. When the attack of the common metal is complete, the liquid is filtered through a small filter and the residue washed thoroughly with hot water. The filter is then incinerated in a porcelain dish or crucible and the ash treated with 2 drops of conc. hydrochloric acid and 1 drop of conc. nitric acid and evaporated to dryness on a water-bath until the excess of acid is entirely expelled. When cold, the residue is taken up in about 2 c.c. of distilled water and filtered, the filtrate being heated to boiling with an equal volume of sulphur dioxide solution or of a saturated oxalic acid solution or a few drops of stannous chloride solution. If gold is present, the characteristic violet-red coloration of purple of Cassius is observed.

**3. Test for Large Objects.**—After removal of any organic matter, the surface is scraped with a penknife and the scrapings submitted to the preceding test.

## SILVER-PLATING

**1. Technical Test.**—The article to be tested, freed from grease,[1] is touched with a drop of conc. nitric acid and the latter absorbed by a strip of filter-paper. The spot is then treated with a drop of formaldehyde solution (commercial formalin) and a drop of 20% sodium hydroxide solution. In presence of silver, a blackish spot of reduced silver forms either immediately or after some time.

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[1] Sometimes objects are covered with a

or a number of small pieces, are treated with 8–10 drops of a
vols. of conc. sulphuric acid with 1 vol. of conc. nitric acid—a
readily dissolves the superficial silver but attacks the metal
ther not at all or but little. When the attack is over, the
ed into a test-tube, mixed with 2–3 c.c. of water, filtered if
divided into two portions. To one of these are added 1–2
e hydrochloric acid, which are allowed to flow gently down
e tube and form a layer on the surface of the sulphuric acid
silver is present, a more or less distinct milkiness is observed
parison with the other portion—at the surface.

**or Large Articles.**—In general the technical test (*see* above)
in this case. If, however, the surface or form of the object
ifficult the surface or a few scrapings may be treated with
ted with an equal volume of water, care being taken to stop
soon as the superficial silver coloration disappears. The
ution is then decanted into a dish and evaporated to dryness
f dilute hydrochloric acid on a water-bath. The residue is
ot water, acidified with nitric acid and filtered through a small,
filter, which is repeatedly washed with hot water. A small
ot, dilute ammonia is then passed a number of times through
he ammoniacal solution divided into two parts, one of which
y acid with nitric acid. In presence of silver a slight precipi-
e or less marked milkiness is observed.

## NICKEL-PLATING

**cal Test.**—The surface of the article is treated with a drop
ochloric acid, a crystal of methylamine hydrochloride being
and heat applied. In presence of nickel, the place attacked
xhibits a blue spot which disappears on cooling.

**hylglyoxime Test** (highly sensitive).—After being freed
he surface of the object is moistened with one or two drops
diluted with an equal volume of water, the acid being sub-
hed into a test-tube, rendered alkaline with ammonia, heated
ered if necessary and treated with two or three drops of 1%
thylglyoxime solution. In presence of nickel, a red precipitate
pink coloration is formed.

is applied to an object of copper or brass, a little of the latter
n would give a brown coloration and thus mask the nickel
such case, after addition of the glyoxime and gentle heating,

The surface of the object or scrapings from it are treated with h chloric acid diluted with an equal volume of water and gently heated. liquid is filtered and treated with a drop of mercuric chloride solut white or grey precipitate of calomel or metallic mercury being form presence of tin.

## ZINC-PLATING

The surface is heated gently with dilute sulphuric acid and the so transferred to a beaker and treated with hydrogen sulphide. The fi liquid is freed from the excess of hydrogen sulphide, treated with a ammonium chloride, rendered faintly alkaline with ammonia, boile again filtered. To the filtrate, acidified with acetic acid, potassium cyanide is added. In presence of zinc, a dirty white flocculent preci forms either immediately or after some time.

## LEAD-PLATING

Scrapings of the surface are treated in a dish with nitric acid, evap to dryness and taken up in a few drops of water. The solution is for lead by means of potassium chromate or iodide.

## ALUMINIUM-PLATING

The surface, or scrapings of it, are heated with 10% sodium hyd solution. The liquid is diluted somewhat, filtered, acidified with chloric acid and made alkaline with ammonia. A white gelatino cipitate is formed in presence of aluminium.

## COPPER-PLATING

### (on Iron)

The object or part of it is treated in the cold with conc. nitri which dissolves the copper but scarcely affects the iron. The solu decanted off, diluted and tested for copper with ammonia.

## BRASS-PLATING

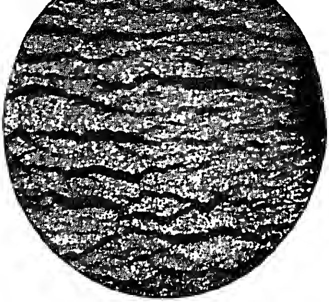


FIG. 28. German sheet

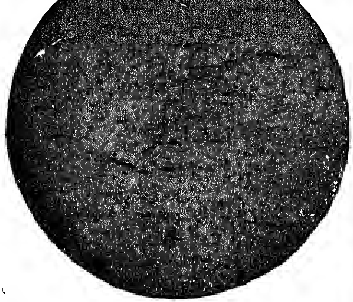


FIG. 29. English sheet

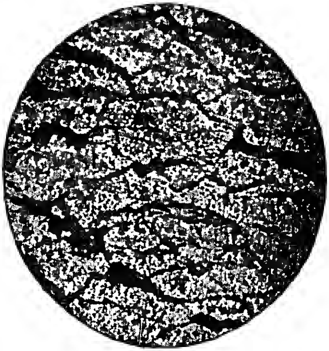


FIG. 30. Belgian sheet

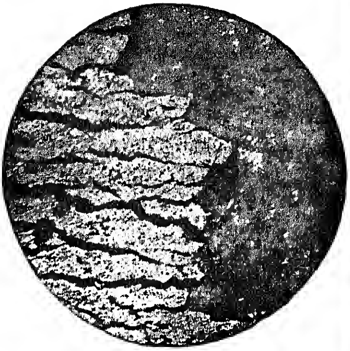
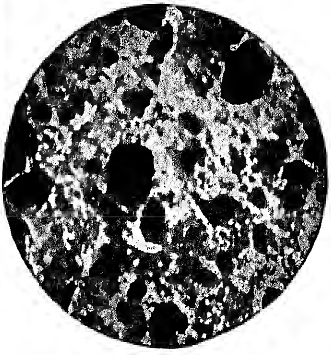
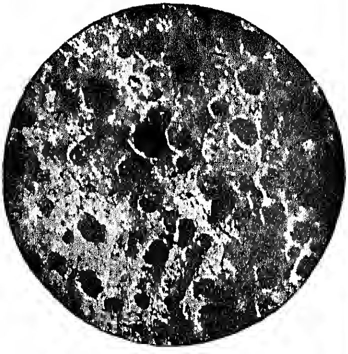


FIG. 31. Belgian sheet (at bend)





a, heated and filtered. In the filtrate, acidified with acetic is tested for with potassium ferrocyanide.

## OXIDISING

sed protection against atmospheric agencies or for the sake , many objects are coated either chemically or mechanically er of oxide, which imparts to them a brown or bluish-brown

oration may, however, arise spontaneously during the working owing to reheating and it is not always easy to decide if the rtificial or spontaneous. One distinguishing character is the l uniformity of the layer of oxide with artificially oxidised nparison with the irregularity of layers of oxide formed spon- e following tests are based on this criterion.

**opper and Brass Objects.**—The surface of the object is eed from grease by means of benzene and treated with a drop ric chloride solution. If the layer of oxide is very regular the reagent will not get into contact with the metal and no e observed. If, however, the oxidation is irregular, the mer- undergoes reduction at the surface of the metal, forming a

**jects of Iron.**—After being cleaned with benzene, the oxidised istened with a drop of 5–6% copper sulphate solution. If 's irregular and hence not artificially formed, a spot of metallic either immediately or after some time, whereas, if the oxida- and uniform, any reduction which may occur will be observable lapse of a long period.

ence to this test it is, however, to be noted that sheet metal *isse*) is now put on the market covered with a regular layer c oxide of a bluish colour, which, although obtained during rolling is very regular and uniform and does not allow of any copper sulphate.

is nevertheless readily distinguishable from that oxidised reagents or the like.

*al test.* When a sheet of this character is bent at right angles e at the bend in the form of scale and shows the naked metal, oxidised by reagents exhibits little change.

*opic test.* Further, microscopic examination, in reflected light agnification of 100–120 diameters, of the surface of such sheet

# CHAPTER VI

# FUELS

ide wood, which is rarely examined as to its value as a com-
uels used industrially are mainly *coal, charcoal* and *mineral* vill be considered later. The coals are distinguished according of carbonisation as *peat, lignite, bituminous coal* and *anthracite.* as a fuel is also made of *coke,* the residue of the dry distillation coal, the volatile products being illuminating gas, ammonia *l-blocks* (briquettes) are also largely used at the present time ; ined by the compression in moulds of fragments of different with the addition of cementing materials. In this way waste tilised and coal which is inconvenient to use on account of ondition rendered more useful.

y and technical value of coal are determined by *chemical* *calorific examination.* The methods adopted are the same nd are described below under the heading : General Methods. part data will then be given relating to each of the different

s, selection of the sample is of great importance.

.—Coal is usually far from homogeneous, and care must be sample for analysis represents as closely as possible the mean f the whole of the parcel to be examined. When the sample from a mine or from a large quantity, portions are taken with different, regularly distributed points of the mass, a large thus collected. The larger lumps of this are broken up and mixed and spread out in the form of a square and the diagonals drawn. Two opposite triangles are then discarded and the , further disintegrated and mixed, formed into another square. ons are repeated several times until a sample of about 2 kilos his being reduced to small pieces and stored in dry, tightly When, however, the laboratory is supplied with a limited ole of the latter is broken up and stored as above.

ase, a portion of the sample thus prepared sufficient for the to be made (about 200 grams) is reduced to coarse powder arately in a dry, air-tight vessel. For each single determina this sample is powdered to the degree of fineness requisite in e being taken not to throw away any part. Consequently, and sieved until the whole has passed through.

# GENERAL METHODS

## 1. Chemical Analysis

This usually includes determinations of the moisture, ash, coke and volatile substances, and sulphur (*see* 1, 2, 3 and 4). Of interest in some cases are determinations of the phosphorus, carbon and hydrogen, nitrogen and oxygen (*see* 5, 6, 7 and 8).

**1. Determination of the Moisture.**—About 5 grams of the substance, not too finely powdered (say, to pass through a sieve of 250 meshes per sq. cm.), are dried in an oven at 105–110° to constant weight, the sample being placed in a covered platinum dish or crucible or between two watch-glasses; as a rule the drying does not require more than two hours. Since dry coal dust, especially that of highly bituminous coal and lignites, tends to oxidise in the air, any increase in weight should be neglected and the preceding weight taken as constant. In such cases, when highly exact determinations are required, the drying should be carried out in a boat in a current of carbon dioxide.

With washed coal, peat and certain earthy lignites, the determination of the hygroscopic moisture is preceded by that of the *water of imbibition.* For this purpose, a large quantity (at least 1 kilo) of the coal, coarsely ground and weighed, is left to dry in the air, the diminution in weight representing the water of imbibition. The substance thus obtained is powdered and used for determining the hygroscopic moisture and other constituents.

**2. Determination of the Ash.**—From 2 to 5 grams of substance (that used for the determination of moisture will serve) are incinerated either in a platinum dish in a muffle or in an open, inclined platinum crucible resting on a perforated asbestos card over a bunsen flame, care being taken to heat gently at first to drive off the volatile substances and to increase the temperature gradually to redness.

In some cases the ash is analysed chemically to determine its principal components and its alkalinity; it may also be examined from the point of view of its fusibility.

**3. Determination of the Coke and Volatile Substances.**—1 gram of the substance (coals rich in volatile matters are best coarsely powdered, say to pass through a sieve of 100 meshes per sq. cm.) is weighed in a platinum crucible 30–35 mm. high, which is placed covered on a triangle of platinum wire arranged so that the bottom of the crucible is 3 cm. above the apex of a bunsen burner giving a flame [illegible] – 0 c[illegible] high. [illegible]he the at of the sulphides) remains in the ash, whilst the remainder lphur and part of that of the sulphides) passes over among of combustion (combustible, injurious or volatile sulphur) xide and, in small proportion, sulphur trioxide.

sulphur is determined by a slight modification of Eschka's is carried out as follows: About 1 gram of the finely (passing a sieve of 650 meshes per sq. cm.) is thoroughly my platinum crucible with about 1·5 gram of a mixture of ide (2 parts) and dry sodium-potassium carbonate (1 part) platinum wire, about 0·5 gram of the same mixture being the top. The open and inclined crucible is then arranged a piece of asbestos board and heated over a small flame so lower portion is reddened. The heating is continued for —the mixture being frequently stirred with a platinum wire ey colour has changed uniformly to yellowish, reddish or rucible is then allowed to cool and the contents washed with a beaker and the liquid made feebly yellow with a little , boiled, and filtered, the residue being washed with boiling ltrate is acidified with hydrochloric acid, boiled to expel free bromine, and the colourless liquid precipitated with e and the barium sulphate weighed as usual.

l and volatile sulphur are required separately, the former is ectly. To this end, a weighed quantity of the coal sufficient ams of ash is incinerated and the ash treated in the hot in a with hydrochloric acid and a little potassium chlorate or idise any sulphites formed as well as the sulphides. The ne or bromine is expelled by boiling, the liquid precipitated and filtered, and the filtrate acidified and precipitated with le in the usual way: $BaSO_4 \times 0{\cdot}1374 = S$. Total sulphur lphur = volatile sulphur.

**ination of the Phosphorus.**—This is carried out on the s), which is digested with conc. hydrochloric acid in a porcelain r-bath, evaporated to dryness and the residue moistened with cid, diluted with water, filtered into another porcelain dish ost to dryness with several additions of nitric acid. The taken up in water acidified with nitric acid and precipitated th ammonium molybdate and so on (*see* Determination of Iron, p. 173).

**ination of the Carbon and Hydrogen.**—These are deter- ordinary method followed for the elementary analysis of nces, th substance being burnt in a current of oxygen and used. About 0·4 gram of substance, not too finely powdered, is used. At the beginning of the combustion, it is well to heat moderately and in a current of air rather than of oxygen; when the volatile products are burnt —this being easily judged from the aspect of the coke remaining in the boat—the fixed carbon is burnt at a high temperature in a current of oxygen. If the undried substance is employed, the moisture content must be allowed for.

**7. Determination of the Nitrogen.**—This is made on 0·75–1 gram of the finely powdered sample by Kjeldahl's method (*see* Fertilisers, p. 123).

**8. Determination of the Oxygen.**—This is calculated by difference, the percentages of carbon, hydrogen, nitrogen, volatile sulphur, ash and moisture being added and the sum subtracted from 100.

## 2. Determination of the Calorific Power

The *calorific power* of a fuel, is the quantity of heat generated by the complete combustion of 1 gram of the fuel, expressed in small calories.

The *small calorie* (*cal.*) is the amount of heat necessary to raise by 1° C. (more exactly from 0° to 1°) the temperature of 1 gram of water. Some refer the calorific power to 1 kilo and use as unit of heat the *large calorie* (*cal.*), which is the amount of heat required to raise by 1° C. the temperature of 1 kilo of water; the numbers are the same in the two cases.

In some cases also the *evaporative power* of a fuel is calculated, this representing the number of kilos of water at 0° which could be transformed into aqueous vapour at 100° by the combustion of 1 kilo of the fuel. Since each kilo of water requires 637 large calories (100 to bring it from 0° to 100° and 537 to transform it into steam also at 100°), the evaporative power is obtained by dividing the calorific power by 637.

The calorific power of a fuel may be calculated approximately from the chemical composition, but it is best to determine it directly by calorimetric methods. The calorific value is referred, according to circumstances, to the fuel as such or simply dried, or to the pure fuel (moisture and ash being deducted).

**1. Calculated Calorific Power.**—Formulæ derived from that of Dulong are used, but the results are only moderately satisfactory. According to Mahler,[1] that to be preferred is the following, which gives, with most coals, errors not exceeding 3%:

$$p = 8140C + 34500H - 3000(O + N),$$

where C, H, O and N are the respective quantities of carbon, hydrogen, oxygen and nitrogen contained in 1 gram of the pure fuel (moisture and ash deducted) and $p$ is the required calorific value, referred to the pure fuel.

of coals with a high degree of approximation is that proposed amely:

$$p = 82C + aV,$$

alorific power of the fuel as such, C and V are the percentages (coke less ash) and volatile matter (less moisture) and $a$ a ressing the calorific power (divided by 100) of the volatile arying with the amount of these volatile matters. To deter- to be ascribed to $a$ the percentage $V^1$ of volatile matters posed free from moisture and ash is calculated by the formula,

the corresponding value of $a$ is then obtained from the

e:

| $a$ | $V^1$ | $a$ | $V^1$ | $a$ | $V^1$ | $a$ |
|---|---|---|---|---|---|---|
| 100 | 14 | 120 | 23 | 105 | 32 | 97 |
| 145 | 15 | 117 | 24 | 104 | 33 | 96 |
| 142 | 16 | 115 | 25 | 103 | 34 | 95 |
| 139 | 17 | 113 | 26 | 102 | 35 | 94 |
| 136 | 18 | 112 | 27 | 101 | 36 | 91 |
| 133 | 19 | 110 | 28 | 100 | 37 | 88 |
| 130 | 20 | 109 | 29 | 99 | 38 | 85 |
| 127 | 21 | 108 | 30 | 98 | 39 | 82 |
| 124 | 22 | 107 | 31 | 97 | 40 | 80 |
| 122 | | | | | | |

**netric Determination of the Calorific Power.**—The r direct methods are undoubtedly to be preferred to those d as they give far more certain results.

ous forms of apparatus devised for such determinations may three classes: (1) calorimeters in which the combustion takes eam of air or oxygen at the ordinary pressure, like those of lbermann, Alexejew, Schwackhöfer, and F. Fischer; (2) n which the combustion occurs with the aid of an oxidising ed with the fuel, as in those of Lewis Thompson, Stohmann, ) calorimeters in which the combustion is effected with oxygen olume and very high pressures, known as *calorimetric bombs*; bomb was due to Berthelot and Vieille and on this were based tical and cheaper ones of Mahler, Hempel and Kroeker, which suitable forms of apparatus for exact determinations.

a mark at two litres, and a brass foot fitted with a small cylindrical copper capsule or furnace in which the combustion occurs. The capsule is covered with a copper cylinder with a row of holes round the bottom and a tube with a tap at the top; this cylinder is held in place by four springs on the brass foot. A thermometer reading to 0·1°, and protected by a metal guard, is also required.

2 grams of the fuel, ground in an iron mortar to pass through a No. 6 sieve (650 meshes per sq. cm.), are thoroughly mixed on a piece of shining paper by means of a flexible steel spatula with the oxidising mixture (3 parts of powdered, dry potassium chlorate and 1 part of potassium nitrate, carefully mixed without using the iron mortar and passed through a No. 6 sieve), sufficient of the latter being used to give a homogeneous, lead-grey mixture, which should burn completely, regularly and moderately rapidly. The amount of oxidising mixture necessary is usually 20–30 grams per 2 grams of fuel, but it varies with the character of the fuel and should be determined by preliminary trial.

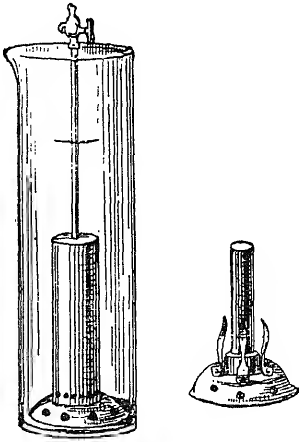


FIG. 34

By means of the spatula used before, the mixture is placed in the copper capsule in such a way as to compress it uniformly and as little as possible; if the quantity of the mixture is too great to be held by the capsule without compression, it is advisable to use only 1 gram of the fuel and the corresponding amount of the oxidising mixture. On the top of the mixture is placed a piece of slow match,[1] which should protrude about a centimetre, the copper cylinder fitted, the tap closed and the whole immersed in the water in the glass cylinder; the water should be, according to circumstances, between 2° and 7° lower than the temperature of the air.[2] The water is mixed by means of the apparatus itself and the temperature shown on the thermometer noted; the apparatus is then withdrawn, the match lighted, the cover rapidly replaced and the whole at once placed in the water before the mixture ignites. After a few seconds, when ignition occurs, the gaseous products issue turbulently from the holes in the cover and escape upward through the water.

burn with difficulty, while peat and many bituminous lignites
ompletely.

hompson calorimeters of English construction, the amount of
the glass cylinder weighs 29,010 grains (1879·85 grams). When
grams) of the fuel are burnt, since 29010 ÷ 30 = 967 = 537
ise in temperature in Fahrenheit degrees (increased by one-
s directly the grains of water at 100° transformable into steam
heat generated by one grain of the fuel, i.e., the evaporative
ed for water at 100° and not, as usual, at 0°.

ointed out that, in England, calorific powers are mostly expressed
e *British Thermal Unit* (B.T.U.), which is the quantity of heat
se the temperature of 1 lb. of water (0·4536 kilo) by 1° Fahrenheit.
ie = 3·9683 B.T.U. and 1 B.T.U. = 0·252 large calorie. Further,
er of $x$ calories per kilo corresponds with 1·8 $x$ B.T.U. per pound,
r pound is equivalent to 0·5555 $x$ calories per kilo.

Thompson calorimeters, the glass cylinder is marked at 2000
2148 c.c. (= 537 × 4). If the latter quantity of water is taken
he fuel are used, the rise of temperature (increased by one-tenth),
e, will give directly the evaporative power (referred to water at
erefore not to the standard usually adopted : *see* later).

R BOMB CALORIMETER. This apparatus (Fig. 35), which is
st of those employed, consists of a vessel or bomb *a* of fairly
nild steel, nickelled outside and enamelled inside : capacity
thickness of walls 8 mm., weight about 4 kilos. The bomb
screwed iron lid *b* with lead packing and furnished in the
ferro-nickel conical screw valve *r*. The cover supports the
sisting of two platinum rods *e*, one passing through the cover
from it and the other fixed directly to the cover and supporting
n dish *c* in which the fuel is placed. The two terminals are
a small spiral of very thin iron wire which burns on passage
(about 2 amps. at 8–10 volts) and so ignites the fuel in contact

rests on supports on the bottom of the brass calorimetric
h contains 2,200 grams of water, a thermometer *t* divided
of a degree and allowing 0·01° to be estimated, and a spiral
protect it from external influences, the calorimeter is placed
e-walled metallic vessel *B* filled with water and covered with

a determination, exactly 1 gram of the fuel, not too finely
weighed into the capsule *c* and this placed in the bomb after
wire spirals has been fitted to the terminals so that it comes
with the fuel. The lid *b* is screwed tightly down, the valve

minutes, ignition is caused by the momentary passage of the current. The temperature is read half a minute after ignition, after a further half-minute, and then each minute until the maximum temperature is reached (after 3 or 4 minutes) and for five minutes during the subsequent fall in temperature.

At the end of the experiment, the tap *r* of the bomb is opened to allow the gas to escape, the bomb itself being then opened and washed out inside with a little distilled water.[2] The nitric acid formed from the nitrogen contained in the bomb is determined in the wash water by titration with caustic potash solution (1 c.c. = 0·01 gram $HNO_3$) in presence of methyl orange. Any sulphuric acid formed is also calculated as nitric acid, but with fuels poor in sulphur no appreciable error is introduced in this way. When, however, allowance is to be made for the sulphuric acid, the procedure is as follows: The wash water is heated for a short time to expel carbon dioxide and titrated with N/10-baryta in presence of phenolphthalein; excess of standard sodium carbonate solution is then added and the excess titrated with N/10-hydrochloric acid in presence of methyl orange. The volume of baryta solution used corresponds with the sulphuric and nitric acids together, and that of the sodium carbonate solution with the nitric acid alone.

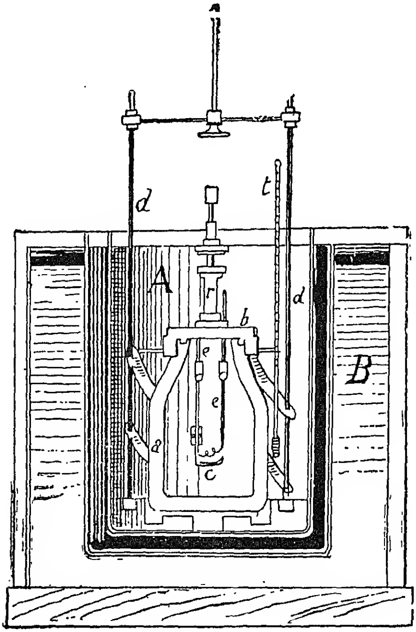


FIG. 35

In calculating the results of the measurement, it is first necessary to establish the correction necessary owing to the exchange of heat with the surrounding air in the interval of time between ignition and the attainment

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[1] Compressed oxygen, if obtained electrolytically, often contains hydrogen, which appreciably alters the results of the calorimetric experiments. In such case it is necessary to purify it, before admitting it to the bomb, by passing it slowly through a red-hot copper tube and then through a coil cooled with water. On the other hand, oxygen from liquid air, containing appreciable quantities of nitrogen, has the disadvantage of giving rise to the formation of nitric acid, allowance for which must be made in calculating the results.

, during every minute of the
n ignition and the attainment of the maximum temperature
ire varies uniformly, so that the correction may be referred
emperature of the minute considered. If the mean tempera-
ite minute differs by less than 1° from the maximum, it is
diminution of temperature due to loss of heat during that
l to the mean diminution in every minute after the maximal
if, however, the mean temperature of any minute differs
imum by more than 1° and less than 2°, the correction for
s taken as the mean diminution after the maximum tempera-
d by 0·005°. Finally, for the first half-minute after ignition
that the variation is equal to the mean observed before the

is correction, account must also be taken of (1) the heat of
the iron coil, 1·6 cal. being allowed per milligram of iron, and
f formation of the nitric acid, which is 0·23 cal. per milligram
(also of the heat of formation of sulphuric acid; in the open
ioxide will be formed and the correction to be subtracted is
milligram of sulphur or 0·73 cal. per milligram of sulphuric

fic power $p$ (in the case where the sulphuric acid has been
nitric acid) is, therefore, expressed by the following formula:

$$p = (T^1 - T + t)(A + a) - 0{\cdot}23n - 1{\cdot}6f \quad . \; . \; . \quad \text{(i)},$$

ved temperature before ignition,
num temperature,
tion for heat given up to surrounding air,
t of water in the calorimeter,
*equivalent* of the apparatus, this being determined once and
or all in a preliminary experiment,[1]
rams of nitric acid formed,
rams of iron in the igniting coil.
s this calculation, it may be pointed out that the various
dicated above compensate one another partly, so that, for

---

*equivalent* is the weight of water requiring the same amount of heat
erature 1° as the calorimetric apparatus (vessel, stirrer, thermometer,
ermined by an experiment with a substance of known heat of com-
aphthalene, 9692; cane sugar, 3957; benzoic acid, 6330 cals.).
etween the true calorific power of the substance and that calculated
mental results without taking account of the heat absorbed by the
led by the rise of temperature, gives the required water-equivalent,
ht desirable to allow for the corrections for the rigorously exact calcu-

corrections are omitted. Under such circumstances the thermo readings during the preliminary period and those after the maximu perature has been passed, and also the titration, becomes useless, t values required being those of the magnitudes in the expression,

$$p = (T^1 - T)(A + a) \; . \; . \; . \; . \; . \qquad \text{(ii)},$$

which then gives the calorific power.

It must also be mentioned that, whilst in the bomb the water (hygr water plus that formed by combustion of the hydrogen in the fuel) in the liquid state, in practice it passes off as vapour among the prod combustion; consequently, the calorific power calculated as above i also the heat of condensation of the water, which in practice is not uti In France the calorific power resulting from the above calculation, presupposing the formation of liquid water (also called *gross calorific p* given, whereas in Germany, Austria, and elsewhere, the heat of conde of the water is deducted, the assumption being made that the water as vapour (*net calorific power*). Taking 600 cals. as the heat of conde of 1 gram of aqueous vapour, if H and M are the percentages of hydrog moisture in the fuel, the deduction to be made from the gross calorific to obtain the net value is 6 (M + 9H). Where an elementary analysis made, a separate determination may be made of the total water evolved the combustion (by burning a given weight of fuel in a tube and collect water in an absorption apparatus), or, as Mahler suggests, in practica mean values of H may be taken according to the quality of the fuel te

EXAMPLE: The experimental data obtained were as follows:

$A = 2200$ grams.
$a = 474$ ,,
$n = 0{\cdot}125$ ,,
$f = 0{\cdot}032$ ,,

Temperature observed:

| | | | |
|---|---|---|---|
| 0 minutes | 15·180° | 7 minutes | 18·250° |
| 1 ,, | 15·185 | 8 ,, | 18·305 ( |
| 2 ,, | 15·190 | 9 ,, | 18·290 |
| 3 ,, | 15·195 | 10 ,, | 18·275 |
| 4 ,, | 15·200 | 11 ,, | 18·260 |
| 5 ,, | 15·205 (ignition) | 12 ,, | 18·245 |
| 5½ ,, | 15·795 | 13 ,, | 18·230 |
| 6 ,, | 17·850 | | |

Hence $T^1 - T = 18{\cdot}305 - 15{\cdot}205 = 3{\cdot}100^\circ$. The law of variation ignition is given by

$$\frac{15{\cdot}205 - 15{\cdot}180}{5} = 0{\cdot}005^\circ,$$

and that after the maximum is passed by

$$18{\cdot}305 - 18{\cdot}230$$

$- 0{\cdot}0325)(2200 + 474) - 0{\cdot}23 \times 125 - 1{\cdot}6 \times 3{\cdot}2 = 8296{\cdot}4$ cals
without corrections according to formula (ii),

$$p = 3{\cdot}1 \times (2200 + 474) = 8289{\cdot}4 \text{ cals.}$$

y the gross calorific power is found. If the fuel contains 3% of ·5% of hydrogen, 6 (3 + 9 × 4·5) = 261 cals., must be subtracted ts to obtain the net calorific power, which is therefore 8035·4 8028·4 (uncorrected).

L'S CALORIMETRIC BOMB. This apparatus, which is simpler han that of Mahler, consists (Fig. 36) of a cylindrical, thick-ron autoclave *A*, holding c. and coated inside with f enamel. It has a screw fits air-tight by means of ad washer and has an ble by a conical screw he lid carries two rods, cted directly with it, and nsulated by means of a g from the lid, through es. Each rod terminates platinum wire bent to a ort a capsule *d* of refrac- which is placed the fuel nto cylindrical form in a ween the two wires is r very thin platinum wire, ates into the cylinder of es the latter when heated a current.

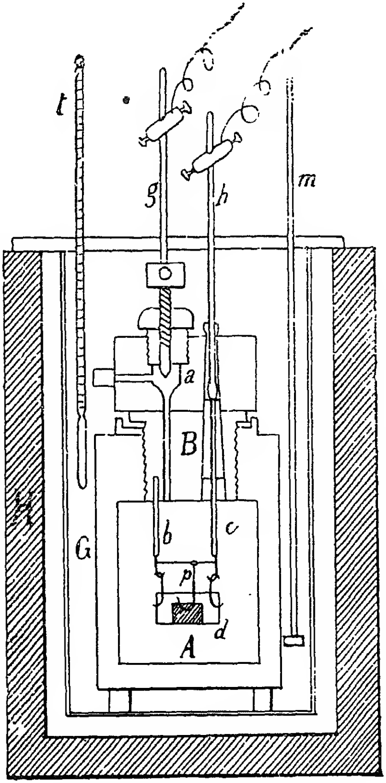

FIG. 36

rimeter is a cylindrical *G* containing, besides the t 1 litre of water and wooden vessel *H* so that between the walls is 2 cm. then closed by a cover, ch pass the two terminals, er *t* to read to 0·01° and a stirrer *m*.

lered fuel is pressed into a cylinder weighing about 1 gram ne igniting wire is already pressed. It is weighed exactly and dish *d* and the bomb closed, oxygen being then passed in slowly ssure becomes abou 15 tmos. The valve *a* is then closed its maximum. The weight of water, plus the water equivalent calorimeter (usually determined once for all by a preliminary measure multiplied by the rise of temperature, gives the heat generated. more exact calculation, the corrections indicated for the Mahler app may be introduced.

Kroeker has modified the Hempel bomb by the addition to the a second valve inserted in a platinum tube leading almost to the of the bomb for the admittance, after the combustion, of a current air into the bomb heated at 105° and the absorption of the expelled vapour in a weighed calcium chloride solution. The amount of th water thus determined is used in calculating the net calorific powe

# SPECIAL PART

## WOOD CHARCOAL

This is distinguished as *hard* or *soft*, according as it is made fron or soft wood, and as *red* or *black* according to the degree of carbon to which it has been subjected. The black, composed principally of c is in the more common use.

⁂

Charcoal contains usually 80–90% C, 1–3% H, 2–4% O, 6–10% $H_2$ 1–3% ash. As a rule, its calorific power lies between 6500 and 7500 ca

## PEAT

This is a fuel of somewhat diverse origins and may, therefore, e very varied aspect and composition. According to its origin, it is guished as *marsh*, *heath*, *meadow*, *forest*, and *marine* peat, and acc to its appearance as mucous, spongy, herbaceous, earthy, compact, l like, etc.

⁂

When freshly extracted, peat always contains a considerable quant water, which may vary from 50 to 90%, whilst, when air-dried, it still co 10–30% of moisture. The percentage of ash varies widely and may be as as 20–30% or even much more.

The best peats have compositions lying between the following limits, refer to the dry product:

in several varieties. Sometimes it has the aspect and colour *wood*) and sometimes it is brown, friable and easy to break *gnite*); in some cases it consists of superposed layers (*schistose* thers is compact and varying in colour from brown to shining *al*).

⁂

won, lignites contain 20–60% of moisture, and when air-dried, ercentage of ash is very variable and, although it usually varies , it may also be much greater. The elementary composition fuel free from ash and moisture, generally varies between the :

| | |
|---|---|
| . . . . . . . . | 55–75% |
| en . . . . . . . . | 4–7% |
| . . . . . . . . | 20–35% |
| n . . . . . . . . | 0·5–2% |

es sulphur may be present in marked proportions. The calorific ignites varies from 4,000 to 6,500 cals.

II (see p. 310) gives the analytical results for various lignites.

## COAL

includes the *bituminous coals* and *anthracite*; there is a on from the one to the other and no sharp delimitation. the most important industrial fuels. They are usually lack, the following types being distinguished: shining, que, black; cannel, of a velvety, blackish colour, with a ure; fibrous coal; and bituminous slates (boghead).

⁂

their chemical composition, coals are classified, after egories, which differ in the quantity and quality of the coke in their calorific powers. The normal limits for each of these ed in Table XXXVIII (p. 311), the data in which are referred (free from moisture and ash).

## TABLE XXXVII

## Composition of Lignites

| Quality. | Chemical Composition. | | | | | | | Fixed Carbon. | Volatile Matters. | Calor Pow |
|---|---|---|---|---|---|---|---|---|---|---|
| | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Moisture. | | | |
| *Italian* | | | | | | | | | | |
| l Gandino, Bergamo) | 36·74–51·46 | 3·72–5·20 | 15·50–26·86 | 0·29–1·38 | 0·84–1.33 | 2·10–23·71 | 12·76–25·95 | 21·17–30·28 | 37·05–54·86 | 4060– |
| oli (Volterra)[1] | 57·16–63·40 | 5·01–5·66 | 25·40–26·68 | | — | 5·54–11·15 | — | — | — | 5168– |
| (do.) | — | — | — | — | 3·86 | 6·16 | 14·55 | 47·46 | 31·83 | 469 |
| na)[1] | 57·38–59·34 | 4·92–5·55 | 28–31·98 | | — | 3·13–9·70 | — | — | — | 532 |
| lo.) | — | — | — | — | 1·71 | 7·82 | 29·78 | 32·75 | 29·63 | 441 |
| nboli (Grosseto)[1] | 73·44 | 6·15 | 15·31 | | — | 5·10 | — | — | — | 748 |
| (do.)[1] | — | — | — | — | 2·34 | 6·00 | — | 60·00 | 34·00 | 600 |
| (do.)[1] | 60·10 | 5·23 | 26·62 | | — | 8·05 | — | — | — | 55 |
| (do.)[1] | — | — | — | — | — | 0·55–7·32 | — | 53·68–61·85 | 37·60–39·00 | 630 |
| e Morgnano (Spol.) | — | — | — | — | 0·87–3·03 | 2·23–22·81 | 36·09–42·59 | 17·85–23·75 | 19·72–38·50 | 1687– |
| s (Gonnesa, Sardinia) | 57·95 | 4·61 | 8·93 | 4·26 | 7·28 | 10·87 | 6·63 | 39·18 | 43·32 | — |
| (do.)[1] | 59·98–70·55 | 4·75–5·25 | 19·40–29·42 | | — | 4·80–5·85 | — | 46·15–55·15 | 42·05–48·00 | 5477– |
| *om other countries* | | | | | | | | | | |
| Germany) (18 samples) | 50·41–55·87 | 3·76–5·23 | 18·00–26·31 | | 0·27–1·78 | 2·28–15·96 | 7·28–16·22 | — | — | 4550– |
| huringia, Anhalt(Germany) ples) | 40·00–58·04 | 3·45–5·98 | 11·13–24·71 | | 0·87–6·03 | 6·94–25·08 | 8·47–23·15 | — | — | 3700– |
| Germany (10 samples) | 43·14–57·73 | 3·43–5·07 | 12·33–25·56 | | 0·44–6·27 | 4·29–19·62 | 9·15–14·36 | — | — | 3870– |
| (10 samples) | 50·32–63·97 | 3·98–5·26 | 5·60–19·06 | | 0·23–10·98 | 2·12–14·28 | 1·13–19·86 | — | — | 4780– |
| yria) | 65·46 | 4·78 | 24·30 | | 1·47 | 4·75 | 0·71 | 46·95 | 47·59 | 62 |
| jan (Hungary) (3 samples) | 44·59–48·02 | 3·59–3·82 | 11·30–12·57 | 0·97–1·06 | 0·99–1·22 | 23·42–26·11 | 11·92–12·00 | — | — | 4165– |
| y (Hungary) | 60·47 | 4·08 | 13·57 | 1·07 | 2·55 | 15·63 | 5·18 | — | — | 56 |
| samples) | 48·94–54·40 | 3·53–4·47 | 10·56–14·90 | | 1·62–4·88 | 15·71–19·25 | 7·95–12·37 | — | — | 4453– |
| (France) | 59·80 | 4·51 | 25·80 | | 1·50 | 6·75 | 3·14 | 45·10 | 45·01 | 55 |
| the Rhone (France) | 63·88 | 4·58 | 11·16 | | — | 12·42 | — | 41·10 | — | 50 |

TABLE XXXVIII

## Limits of Composition of Coals (Gruner)

(The values refer to dry, ashless coal)

| | Elementary percentage Composition. | | | Ratio $\frac{O+N}{H}$ | Percentage of | | Appearance and quality of the Coke. |
|---|---|---|---|---|---|---|---|
| | C | H | O+N | | Coke (fixed carbon) | Volatile Matters. | |
| ame<br>cak- | 75–80 | 5·5–4·5 | 19·5–15·5 | 4–3 | 50–60 | 50–40 | Pulverulent or only slightly coherent. |
| ame | 80–85 | 5·8–5 | 14·2–10 | 3–2 | 60–68 | 40–32 | Caked but very porous. |
| or | 84–89 | 5·5–5 | 11–5·5 | 2–1 | 68–74 | 32–26 | Caked, somewhat porous. |
| ame<br>oal | 88–91 | 5·5–4·5 | 6·5–4·5 | about 1 | 74–82 | 26–18 | Caked and compact. |
| ame<br>coal | 90–93 | 4·5–4 | 5·5–3 | about 1 | 82–90 | 18–10 | Adherent or pulverulent. |
| . | 93–95 | 4–2 | 3 | about 1 | more than 90 | less than 10 | Pulverulent. |

power of coals, referred to the dry, ashless fuel, varies in general
oo cals.

e uses to which different coals are especially suited, long flame,
(Class 1) is adapted to the manufacture of gas and particularly
furnaces. Gas coal (Class 2) is preferred for making gas, since,
ith the preceding, it gives volatile matters richer in carbon
illuminating, although in lower yield. Fat, caking or furnace
or use in reverberatory furnaces and for making metallurgical
ter purpose the short-flame caking coals are particularly adapted.
, short-flame or anthracitic coals and the anthracites, owing
bustion and to the little smoke they give, are used for domestic
r the heating of boilers, where a slow, quiet fire is required.
equence of the paucity of their volatile matters, the anthracites
ectly in blast furnaces instead of coke.

l purposes coal should not contain more than 2–3% of sulphur.
ntain 3–8% of ash and the proportion may be 12% in good
h more than this is regarded as medium or bad. The moisture
l should not exceed 3%.

X gives the analytical results for a number of bituminous coals

TABLE XXXIX

## Compositions of Different Coals

| | Chemical Composition. | | | | | | | Coke. | Volatile Matter. | Calorific Power. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Moisture. | | | |
| *British* | | | | | | | | | | |
| Abercarn : caking coa . . . | 84·77 | 4·98 | 4·66 | | 0·55 | 4·14 | 0·90 | — | — | — |
| estern Valley : ,, . . . | 83·64 | 4·59 | 7·01 | 1·06 | 0·71 | 2·23 | 0·76 | — | — | 8058 |
| llery : ,, . . . | 82·32 | 4·75 | 4·59 | | 1·03 | 6·59 | 0·72 | — | — | — |
| sca : ,,[1] . . . | 83·25 | 4·96 | 3·40 | 1·65 | 0·79 | 5·95 | — | 68·9 | — | 7956 |
| xon's Navigation : Anthracitic[1] | 90·27 | 4·12 | 2·53 | 0·63 | 1·20 | 1·25 | — | 84·5 | — | — |
| rndale : ,, | 89·10 | 4·75 | 2·06 | 1·20 | 0·85 | 1·40 | 0·64 | 86·5 | — | 8131 |
| mbrian Navigation : ,,[1] | 90·06 | 5·16 | 2·79 | 0·79 | 0·58 | 0·62 | — | 86·5 | — | — |
| bion Merthyr : ,, | 88·30 | 4·56 | 2·78 | 1·50 | 0·98 | 1·20 | 0·68 | 84·6 | — | 8080 |
| nrikyber Navigation : ,,[1] | 90·41 | 4·82 | 1·71 | 0·96 | 0·71 | 1·39 | — | 89·1 | — | — |
| eat Western Nav. : ,, | 86·48 | 4·04 | 3·62 | 0·88 | 0·70 | 3·04 | 1·24 | 81·5 | — | 7755 |
| ll's Plymouth, Merthyr: ,,[1] | 89·49 | 4·00 | 3·78 | | 0·84 | 1·89 | — | — | — | — |
| iental Merthyr : ,, | 86·36 | 4·78 | 2·21 | 1·37 | 0·71 | 3·69 | 0·88 | — | — | 7964 |
| ysfaio Merthyr : ,, | 84·20 | 3·90 | 2·49 | 1·17 | 0·96 | 6·65 | 0·63 | 85·2 | — | — |
| wys Merthyr : ,, | 86·40 | 4·05 | 1·97 | 1·10 | 0·96 | 4·57 | 0·95 | 84·7 | — | 7956 |
| aval Merthyr : ,, | 88·83 | 4·63 | 2·02 | 1·10 | 0·50 | 2·60 | 0·32 | 85·7 | — | 8080 |
| andard Merthyr : ,, | 87·21 | 4·11 | 1·75 | 1·60 | 1·05 | 3·68 | 0·60 | — | — | — |
| Peacock : Anthracitic[1 2] . . | 90·61 | 3·77 | 2·32 | | 0·98 | 2·28 | — | 91·52 | 6·20 | 8589 |
| ercrave : ,,[1 2] . . | 91·25 | 3·60 | 2·32 | | 0·83 | 2·00 | — | 92·04 | 5·96 | 8541 |
| rydail : ,,[1 2] . . | 91·60 | 3·61 | 3·25 | | 0·44 | 1·10 | — | 93·60 | 5·30 | — |
| nville's Court ,,[1] . . | 94·18 | 2·99 | 0·50 | 0·76 | 0·59 | 0·98 | — | — | — | — |
| w Main : Gas coal . . . | 82·58 | 4·42 | 6·64 | 0·85 | 0·81 | 3·47 | 1·23 | 71·6 | 28·4 | — |
| lton : ,, . . . | 84·93 | 5·13 | 4·92 | 1·53 | 1·14 | 1·48 | 0·87 | 69·6 | 30·4 | — |
| on : ,, . . . | 84·06 | 5·11 | 6·34 | 0·75 | 0·82 | 1·36 | 1·56 | 67·8 | 32·2 | — |
| : ,, . . . | 82·36 | 5·11 | 6·56 | 1·05 | 0·86 | 2·04 | 2·02 | 66·7 | 33·3 | — |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ayrshire : Main, Steam coal[1] | 79·82 | 5·82 | 11·31 | 0·94 | 0·86 | 1·25 | — | 49·3 | 50·7 | — |
| Lesmahagow : Cannel coal[1] | 73·44 | 7·62 | 11·77 | | 1·14 | 6·03 | — | 43·3 | — | — |
| Edinburgh : Boghead[1] | 63·10 | 8·91 | 7·25 | | 0·96 | 19·78 | — | — | — | — |
| *German and Austrian* | | | | | | | | | | |
| : Silesia (128 samples) | 55·46–81·50 | 3·82–5·38 | 5·19–15·23 | | 0·29–2·80 | 1·77–23·68 | 0·70–7·99 | — | — | 555 |
| · Silesia (24 samples) | 61·89–79·26 | 0·56–4·86 | 1·74–12·33 | | 0·74–1·67 | 6·13–33·85 | 0·81–4·93 | — | — | 512 |
| : Provinces and Westphalia (38 samples) | 58·82–84·24 | 3·83–5·48 | 2·13–11·25 | | 0·71–4·77 | 3·04–23·52 | 0·42–7·04 | — | — | 659 |
| Basin (5 samples) | 63·00–76·97 | 4·00–4·97 | 6·57–10·12 | | 0·79–1·12 | 9·36–24·12 | 1·01–4·56 | — | — | 600 |
| ty (7 samples) | 53·04–76·62 | 3·13–4·91 | 7·75–10·80 | | 1·03–2·24 | 5·25–31·04 | 2·65–6·23 | — | — | 495 |
| nia (6 samples) | 64·09–70·63 | 3·65–4·83 | 8·42–17·24 | | 0·92–1·03 | 2·58–10·98 | 5·90–10·65 | — | — | 602 |
| *French* | | | | | | | | | | |
| (Nord) : Caking coal[2] | 83·75 | 4·39 | 5·76 | | — | 5·00 | 1·10 | 73·70 | 20·20 | 8 |
| (Pas de Calais) : Caking coal[2] | 87·74 | 4·68 | 5·03 | | 0·86 | 1·55 | 1·00 | 78·45 | 19·00 | 8 |
| do. Gas coal[2] | 83·73 | 5·22 | 7·00 | | — | 3·00 | 1·05 | 66·40 | 29·55 | 8 |
| ny (St. Etienne) : Gas coal[2] | 81·27 | 5·31 | 8·59 | | — | 3·60 | 1·23 | 64·70 | 30·47 | 8 |
| d' Combe (Gard) : Coke coal[2] | 87·16 | 4·27 | 4·16 | | — | 3·80 | 0·61 | 82·80 | 12·79 | 8 |
| ty (Côte d'Or) : Non-caking, long-flame l[2] | 74·73 | 5·17 | 11·75 | | 1·28 | 4·85 | 3·50 | 55·55 | 36·10 | 7 |
| ot (Côte d'Or) : Anthracitic coal[2] | 89·39 | 3·66 | 3·70 | | — | 1·45 | 1·80 | 86·65 | 10·10 | 8 |
| nentry (Allier) : Gas coal[2] | 80·18 | 5·25 | 8·17 | | 0·59 | 3·40 | 3·00 | 56·20 | 37·40 | 7 |
| : Anthracite[1] | 94·00 | 1·49 | 0·85 | | — | 3·66 | — | — | — | — |
| *Belgian.* | | | | | | | | | | |
| Buisson (Mons) : Caking coal[1] | 83·40 | 5·40 | 7·76 | | — | 3·44 | — | — | — | — |
| Vue (Mons) : Short-flame, caking coal[1] | 86·38 | 4·48 | 6·09 | | — | 3·05 | — | — | — | — |
| Martin (Charleroi) : ,, ,,[1] | 86·23 | 4·62 | 5·81 | | — | 3·34 | — | — | — | — |
| let (Charleroi) : Anthracitic coal[1] | 90·89 | 3·65 | 3·98 | | — | 1·48 | — | — | — | — |

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[1] In these analyses the numbers refer to the dry fuel; in the others to the fuels as they stand.

[2] In these analyses the numbers in the *Coke* column represent fixed carbon (coke minus ash).

TABLE XXXIX (*continued*)

## Compositions of Different Coals

| | Chemical Composition. | | | | | | | Coke. | Volatile Matter. | Ca P |
|---|---|---|---|---|---|---|---|---|---|---|
| | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Moisture. | | | |
| *Russian* | | | | | | | | | | |
| (16 samples) . . . . . . . . | 51·42–70·54 | 3·54–4·81 | 10·18–15·43 | | 0·72–2·37 | 4·26–27·48 | 4·71–9·63 | — | — | 480 |
| henkowo (S. Russia): Caking coal . | 81·52 | 4·81 | 12·94 | | 0·74 | 0·73 | — | — | — | |
| *American* | | | | | | | | | | |
| lvania (3 samples) [1] . . . . . . | 76·60–80·10 | 4·35–4·61 | 8·41–10·22 | 1·05–1·10 | 0·65–1·30 | 5·38–6·35 | — | — | — | |
| (2 samples) [2] . . . . . . . . | — | — | — | | 0·97–0·98 | 5·87–7·24 | 0·71–1·47 | 63·66–76·83 | 16·59–27·63 | 78 |
| rn Virginia (3 samples) [2] . . . . . | — | — | — | | 0·46–1·65 | 3·14–4·63 | 0·47–0·80 | 62·33–81·59 | 14·80–32·24 | 81 |
| (2 samples) [2] . . . . . . . . . | — | — | — | | 0·48–0·95 | 5·68–8·58 | 4·00–7·67 | 57·69–58·56 | 28·86–28·96 | 69 |
| lvania: Anthracite [2] . . . . . | — | — | — | | 0·46–1·03 | 4·38–11·23 | 1·30–4·12 | 80·87–87·98 | 3·08–8·10 | |
| do. [2] . . . . . . . . . . . | 86·45 | 2·00 | 2·20 | | — | 5·90 | 3·45 | 87·93 | 2·72 | |
| *Asiatic* | | | | | | | | | | |
| (6 samples) [2] . . . . . . . . . . | — | — | — | | 0·23–0·53 | 1·82–6·86 | 1·42–2·45 | 45·87–53·42 | 43·18–48·71 | |
| (4 samples) . . . . . . . . . . | — | — | — | | 0·34–4·34 | 8·90–19·80 | 0·60–4·70 | 57·85–76·80 | 8·30–31·68 | 68 |
| *Italian Anthracites* | | | | | | | | | | |

tıng coke, obtained as a secondary product in the manu-
iinating gas from long-flame bituminous coal, forms more
highly porous lumps of a grey colour. Metallurgical coke,
ed from a fat, short-flame coal, is resistant, sonorous and
metallic lustre. In every case, coke consists, apart from
of carbon.

⁂

oke should contain only 1–2% of moisture; if washed and air-
tain as much as 5–6%. With certain cokes the ash may amount
od samples usually contain 4–10%.
e usually contains 83–90% C, 0·3–2% H, 2–6% O and 1–2%
on of sulphur may reach 2·5%, but for metallurgical coke the
nt is that it shall not exceed 1%. With cokes not excessively
calorific power varies from 7000 to 8000 calories.
t is required that a good metallurgical coke should not contain
of water, 8% of ash and 0·5% of sulphur, and that its calorific
e about 8000 cals.

## AGGLOMERATED FUELS

### (Briquettes)

in quality with the coal and agglutinating material used
acture. Bituminous coal is the more commonly employed
stly taken to act as cohesive, although many other materials
oosed.
are usually brick-shaped, but cylinders, sometimes per-
tate access of air, and ovoid forms are also made
fuels, in addition to the determinations given under the
ral methods," it is important to ascertain the *cohesion or*
This may be done with a special apparatus, or by a crushing
the largest face (with brick-shaped briquettes).
ses also the *resistance to heat* is tested, in order to find out
s soften when kept for a certain time at a definite tempera-
ours at 60°).
*nation of the pitch* used as agglutinant may be carried out
by extraction in a Soxhlet apparatus with carbon disulphide
ceases to become coloured (this usually requires at least
porating the carbon disulphide and weighing the residue

to that of the good coal from which they are made and in general should not be below 7500 cals.

## CHAPTER VII

# COAL TAR

## AND ITS PRODUCTS

dry distillation of coal, as in the manufacture of illuminating e preparation of coke, *crude tar* is collected as a secondary en subjected to further treatment this gives, on distillation, being distinguished according to the temperature at which ted, as *light*, *medium*, *heavy* and *anthracene oils*. The residue lation is *pitch*. From the light oils are obtained, by further *nzene* (benzole) and the *toluenes* (toluoles), which are used in xplosive industries and as solvents. The medium, heavy e oils yield other products of industrial importance, such as *thracene*, *carbolic acid*, *pyridine bases* and *impregnating oils*. oducts are considered separately in succeeding paragraphs, nonly made in each case being indicated.

—With very viscous liquids, such as crude tar and heavy e oils, it is not easy to obtain a sample exactly representing position of the whole mass. To take such a sample from the containing the material, use is made of a metallic dipping n. wide and closed at the bottom by a plug which is raised means of an iron wire passing through the cylinder itself. filled several times and all the samples mixed so as to obtain ve a sample as possible. With a non-viscous liquid, however, o mix the mass before extracting the sample.

products such as naphthalene and anthracene, the mass ned to see if it is all of the same appearance, and samples wn from different parts and mixed before analysis.

## CRUDE TAR

nse, black, oily liquid with a characteristic odour due to the omatic hydrocarbons, phenols, naphthalene and pyridine It is to be distilled, the tests made are 1–4 (below), but if it is fuel, the ash content and the calorific power are determined l oils (*q.v.*).

**ination of the Water.**—Since tar exhibits a tendency to er present to separate, either the sample should be taken subsequent determination being suitably increased.

In a glass or copper distillation flask, a weighed quantity of 100 of the well-mixed sample is distilled with 50 c.c. of benzene (90% and through a condenser. The distillation is carried up to 190° in abou an hour, the distillate being collected in a graduated cylinder and the v of the aqueous layer read off. Industrially, the water is determined d during the distillation test and is collected with the light oils, from it separates on standing, so that it may be easily measured.

**2. Determination of the Specific Gravity.**—The tar is first pletely freed from water. To this end it is left for 24 hours in a closed in a bath of water heated to a temperature not higher than 50°, being s from time to time to facilitate the rising of the drops of water a bubbles. When the layer of water is thoroughly separated, it is de or siphoned off and the specific gravity of the residual tar determi 15° C. With a fairly mobile tar, an ordinary densimeter or picnom used, but with very dense tar either a picnometer for solids, with mouth and a ground stopper surmounted by a tube with a mark o an ordinary weighing bottle with a rill in the stopper[1] may be use

**3. Determination of the Free Carbon.**—According to K method,[2] 10 grams of the tar are boiled with 25 c.c. of acetic acid c.c. of toluene in a conical flask with a reflux apparatus and the hot filtered through two filter-papers reduced to equal weight and plac inside the other. The residue on the filter is washed with hot toluen the latter passes through colourless, the two filters being then sep and dried at about 120° until of constant weight. The difference in between the two filters gives the free carbon.

From the content of free carbon ($c$) thus obtained, the yield o in pitch of a definite hardness may be determined—knowing the prop $k$, of free carbon in the pitch—by the formula $x = \frac{100\,c}{k}$.

Assuming that, for a good pitch of medium hardness, $k$ is 28%, a t taining $c$% of free carbon will give $x = (100c \div 28)\%$ of such pitch.

**4. Fractional Distillation.**—Fractional distillation of tar p difficulties on account of the bumping, which is due mainly to the p of water. It is, therefore, necessary first to dehydrate the tar as com as possible in the manner indicated above, then to distil from a fla more than half full and to heat with great care until all the residua is eliminated. The apparatus used for the distillation of mineral oi be employed (*see* Chapter VIII). It is also advantageous to pass t the boiling liquid a gentle current of air by means of a capillary tube ng over become intensely red. The residue in the retort, pitch, is weighed.

he distillation test is carried out on larger quantities (0·5 to allic vessel, so that results in greater accord with those of the btained.[1]

⁂

ravity of coal tar (dry) usually varies from 1·100 to 1·280, but ses may be below 1. The composition of the tar varies according of the coal yielding it and to the mode of heating (whether in ontal retorts), and similar variation is shown by the yield of ucts. Tar contains 10–35% of free carbon and the quantity sible in it when sold to the distilleries is 4–5%.

## CRUDE LIGHT TAR OILS

these products includes the following determinations :

**nation of the Specific Gravity.**—By means of a hydrophal balance at 15° C.

**ion.**—100 c.c. are fractionally distilled from a glass per vessel of 150 c.c. capacity, furnished with a theronnected with a condenser. The portion passing over up rude benzole (with toluole, etc.) and that between 120° and ha (*solvent naphtha*) ; the residue is regarded as middle oils. ay be tested by the reactions for detecting the presence troleum oils (benzine) or oil of turpentine (*see* later : Benzole, Oil of Turpentine, Vol. II).

**nation of the Phenols.**—The fractions obtained from istillation are reunited, the containing vessels being rinsed and the whole introduced into a 500 c.c. graduated cylinder stopper and repeatedly shaken with 100 c.c. of caustic soda ). After being left at rest for some time, the volume of underneath is read, the increase in its volume giving the phenols by volume.

exact determination the alkaline layer is collected and a water-bath until addition of water no longer produces en cold, the liquid is acidified with hydrochloric acid and dium chloride, the layer of phenols which separates being

**ination of the Bases.**—The oil freed from phenols by the described is repeatedly shaken with 30 c.c. of 20% sulphuric

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chnical Methods of Chemical Analysis (London, 1911), Vol. II, p.

giving the percentage by volume of the bases. These may also be
mined directly by collecting the acid liquid, carefully adding to it
excess of caustic soda solution (D 1·40), and measuring the bases
separate.

⁂

The specific gravity of the light oils usually lies between 0·900 and
Normal oils give about 90% of distillate up to 200° and have the specific
0·930; they contain 5–15% of phenols and 1–3% of bases.

## MIDDLE AND HEAVY TAR OILS

With these the following determinations are made:

**1. Determination of the Specific Gravity.**—As with light oi

**2. Distillation.**—This is carried out either with the product
stands, which is distilled from a flask with a long side-tube but no con
(to prevent crystallisation of naphthalene), or with the product fre
naphthalene, or with that free also from phenols and bases, resultin
determinations 3 and 4.

**3. Determination of the Crude Naphthalene.**—From 0·5 to
of the oil is left for 24 hours at 15° and then cooled if necessary to
the naphthalene to crystallise, this being pumped off on a cloth or
filter, pressed in a press until all the oily part is removed and we
This represents the crude naphthalene, of which the melting and
points may be determined.

**4. Other Determinations.**—The oil free from naphthalene is t
with caustic soda to determine the phenols, and with dilute sulphur
to determine the pyridine bases, as with the light oils (3 and 4).

⁂

A *good middle oil* has a specific gravity not less than 1; at least 90
distil below 260°, and it contains not less than 30% of crude naphthalen
210–220°). The naphthalene-free oil has the specific gravity 0·99–1·0
contains 25–35% of phenols (about one-third of this being carbolic aci
about 5% of bases.

The *heavy oils* have a mean specific gravity 1·04 and distil betwee
and 300°; they contain mainly naphthalene and other solid hydroca
together with 8–10% of phenols (principally cresols and higher homo
and about 6% of pyridine bases.

## ANTHRACENE OILS

The analysis of anthracene oils includes, besides determinations
specific gravity and of the behaviour on distillation—which are c
out as with the middle oils, only the determination of the anthr

hard pitches should first be powdered.

**nation of the Free Carbon.**—As with tar (*see* Crude Tar,

**nation of the Ash.**—2 or 3 grams of the pitch are burnt rucible in a muffle and the residue weighed.

**ination of the Volatile Matter and Coke.**—As with fuels portant to note the appearance of the coke—whether swollen, ked.

**g and Melting Temperatures.**—These serve better than ndicate the degree of purity of the pitch. In a beaker of g about half a litre of water is suspended a cube of the pitch n. side or a disc 4–5 mm. thick at the end of an iron wire, 5 cm. from the bottom. A thermometer is immersed with same depth as the pitch and the temperature of the water nute. From time to time the pitch is withdrawn to ascertain s when pressed between the fingers. The *temperature of ng* is taken as the lowest at which the pitch can be twisted g, while the *temperature of softening* is that at which it can ween the fingers without force and the *melting point* as that gins to drop.

**on between Tar Pitch, other Pitches and Natural** characters of these products are as follows:

| Vegetable Pitch (Black or Marine Pitch). | Petroleum Pitch. | Stearine Pitch. | Natural Bitumen. |
|---|---|---|---|
| Black, with an odour recalling that of vegetable tar. | Black, almost odourless. | Black, odour of fatty substances. | Blackish, usually solid and hard, sometimes soft. |
| Very soluble in alcohol, giving a brown solution containing resinous matters and giving the reactions for phenols. It colours potash solution brown. | Almost completely insoluble in petroleum ether. | Insoluble in alcohol and partially soluble in petroleum ether. | Insoluble in alcohol; does not give the reactions for phenols. |
| The distillate has an acid reaction. | In general has no saponification number. | Has a saponification number and an acid number. | |

carbon content is rarely less than 25–30%, and for that from vertical retorts or blast-furnaces, 5–7%. The ash content is less than 0·5% for gas pitch and more than 1% (6–10%) for that from blast-furnaces. The yield of coke varies from 30 to 60%, and the coke has a more or less porous appearance according to the type of pitch from which it is derived (very porous with the very hard pitches, less so with the others).

As regards the temperatures of softening and fusion, the following limits may be taken for different types of pitch:

*Soft:* Softens at 40°, melts at 50–60°.
*Hard:* Softens at 60°, melts at 70–80°.
*Very hard:* Softens at 80–85°, melts at 90–120°.

A good pitch for making briquettes should, according to Spilker[1] have the following properties: not more than 0·5% of ash; softening point between 60° and 75°; solubility in aniline, 70–75%, and in carbon disulphide, not less than 70%; yield of coke, 45%; appearance of coke, caking and not too much swollen.

## IMPREGNATING OILS

These are usually creosote oils or anthracene oils, freed more or less completely from crystallisable substances, and are used for the impregnation of wood, especially railway sleepers and telegraph poles, with the object of preserving it.

In general they are brownish red or blackish liquids, more or less fluorescent, somewhat viscous, and with a more or less marked odour of the products of tar distillation.

The principal tests to be made are:

**1. Determination of the Specific Gravity.**—By means of a hydrometer or Westphal balance at 15° C.

In some cases measurements are made at higher temperatures, e.g., at 25, 45, 50° C.; the temperature used must be indicated in the report.

**2. Distillation.**—This is carried out in a tubulated retort of about 300 c.c. capacity, furnished with a thermometer. The retort is charged with 100 c.c. of the liquid and the thermometer bulb arranged at about 2 cm. from the liquid, which is heated so that 120 drops per minute pass over; the different fractions are measured.

**3. Determination of the Phenols and the Naphthalene.**—The fractions obtained as under 2 are reunited in a graduated cylinder, shaken repeatedly with 100 c.c. of caustic soda solution (D 1·15) saturated with sodium chloride and then left to settle; the increase in volume of the soda solution gives the percentage of phenols. In the supernatant oily layer the naphthalene is determined by cooling (to 15°) in the manner indicated

nay also be required ; these are ascertained as with heavy
*ee* these : Chapter VIII).

⁂

sition of impregnating oils varies according to the conditions of
Thus, a specific gravity of 1·03–1·10 or of 1·05 at 50° is required :
30% of naphthalene ; a content in phenols of 5–10%, and various

## BENZOLES

l benzoles from the tar industry are mixtures in varying
benzene, toluene and xylenes, and contain also ethylbenzene,
enes and other homologues of benzene. The separate pure
are obtained by
complicated rectifica-

ed benzoles are colour-
quids with a character-
odour ; any turbidity
ence of water.
and determinations to

**rmination of the**
**vity.**—By the West-
densimeter or picno-

**ation.** — This test,
to characterise com-
les, may be carried
inary distillation flask,
t used for light mineral
ially, however, the de-
tions given by Krae-
er[2] are followed, so
ble results may be

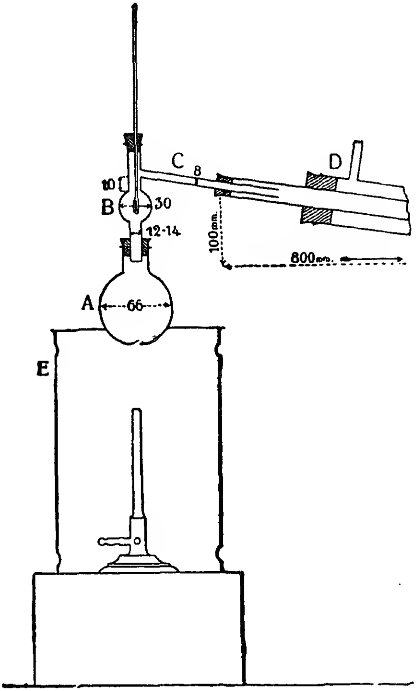


Fig. 37

tion apparatus used is
Fig. 37 and consists of a copper vessel *A*, 0·6–0·7 mm. thick,
in capacity and of the dimensions indicated. To the mouth
is fitted a dephlegmator *B*, 14 mm. wide and 150 mm. long,
a bulb, nd with a side-tube 8 mm. in diameter, fixed almost

The lateral tube of the dephlegmator is connected with a condenser *D*, 800 mm. long, inclined so that the top end is 100 mm. higher than the free end.

With this apparatus 100 c.c. of the liquid are distilled in such a manner that 5 c.c. distil over per minute (2 drops per second), fractions passing over at different temperatures (up to 100°, 120°, 145°, 160°, 175°, 190°, according to the different types of benzole) being collected in a graduated cylinder and measured.

For exact determinations it is necessary to take account of the atmospheric pressure, bearing in mind that for pressures between 720 and 780 mm. the percentages given by the distillation should be diminished by 0·033 for 90% benzoles and by 0·077 for 50% benzoles for each millimetre of pressure below the normal pressure of 760 mm. and increased by the same amounts for each millimetre above 760 mm.

**3. Determinations of the Separate Hydrocarbons.**—To separate and estimate approximately the different hydrocarbons contained in commercial benzole, the latter must be fractionally distilled in a manner rather different from that just described, a moderately large amount of substance being treated in an apparatus furnished with an efficient dephlegmator. Use is generally made of a copper vessel of the form and dimensions indicated (in millimetres) in Fig. 38, a six-bulb Le Bel-Henninger fractionator, 60 cm. long, being fitted to it. The fractionator is provided with a thermometer and joined to a condenser, and 1 kilo of the product is distilled at the same rate as in 2 (above), the different fractions being collected in tared receivers, which are subsequently reweighed.

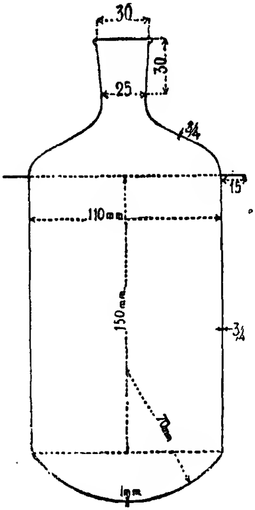


FIG. 38

The separation of the different hydrocarbons may be effected by further fractional distillations, regard being paid to the boiling points, which are as follows: benzole, 80–81°; toluole, 110–111°; xyloles, 138–142° (*o*-xylene, 142°; *m*-xylene, 139–140°; *p*-xylene, 138–139°); ethylbenzene, 137°; trimethylbenzenes, 163–175°.

The fractionation of the different commercial products is carried out on the basis of the following temperature limits:

| | Benzole (50% and 90%): | Pure commercial Benzole. | Toluole. | Xyloles. |
|---|---|---|---|---|
| First fraction . . | up to 79° | up to 79° | up to 109° | up to 135° |
| Benzole . . . | 79–85 | 79–81 | | |
| Intermediate fraction . | 85–105 | | | |

ted by means of fractional distillation, their boiling points being he respective quantities may, however, be determined approximarding the distillate between 135° and 137° as *p*-xylene, that nd 140° as *m*-xylene, and that between 140° and 145° as *o*-xylene ; er to uncorrected temperatures, i.e., those indicated by a therits scale only partially immersed in the vapour.

**n and Estimation of Impurities.**—The impurities of nzoles are principally carbon disulphide, thiophene, paraffin and naphthalene.

N DISULPHIDE. This is *detected* by shaking about 10 c.c. of , better, of the first fractions of its distillate, with 5 or 6 drops azine and leaving the mixture at rest for an hour. In presence ·2% of carbon disulphide, a white precipitate of phenylhydralphocarbazinate is formed.

*termination*, the ammonium xanthate (Hoffmann) reaction is

of 50 grams of the benzole with 50 grams of alcoholic potash rams of KOH in 90 grams of absolute alcohol) is left for some rdinary temperature and is then shaken with 100 c.c. of water. layer is separated from the benzole, which is washed two or ith water, the total aqueous liquid being made up to 400 c.c. n, or an aliquot part of it, the potassium xanthate formed is lumetrically by means of a standard copper solution (12·468 tallised copper sulphate per litre).

cted by acidifying the aqueous liquid containing the xanthate cid and then adding the copper sulphate solution until the xcess, i.e., until a drop of the liquid gives the brown coloration m ferrocyanide. The number of c.c. used, multiplied by the percentage of $CS_2$ in the aqueous liquid and from this the the benzole may be calculated.

HENE. This is *detected* by the indophenine reaction. To a f isatin in a porcelain basin, a few c.c. of pure conc. sulphuric d and then the benzole, the liquid being covered with a clockto itself for some hours : in presence of thiophene, blue rings the isatin granules.

les guaranteed free from thiophene are tested for the latter.

FIN HYDROCARBONS (benzines). These are *determined* by the benzoles into the soluble sulpho-acids (Kraemer and Spilams of the benzole are shaken for 15 minutes in a separating

For exact determinations, the hydrocarbons remaining suspended in the sulphuric acids employed should be collected. The acid liquors are poured slowly and with shaking on to an equal weight of pounded ice in a flask, the temperature never exceeding 40°. The liquid thus obtained is distilled and the oil separating at the surface of the first 50 c.c. of distillate added to the quantity determined directly. The total oil thus obtained is repeatedly purified with fuming sulphuric acid (20% of anhydride) in lots of 30 grams each until no further diminution in volume takes place. It is then washed with water and measured, the volume, divided by 2, giving the quantity of paraffin hydrocarbons in 100 of the benzole.

(*d*) NAPHTHALENE. 10 c.c. of the benzole are allowed to evaporate spontaneously in a glass dish, any naphthalene present remaining crystallised on the walls of the dish.

**5. Degree of Refining.**—Benzoles may contain larger or smaller quantities of resinous substances not completely removed by refining. The presence of these substances may be detected as follows:

(*a*) WITH SULPHURIC ACID. 5 c.c. are added to 5 c.c. of conc. sulphuric acid in a cylinder with a ground stopper, the mixture being shaken for two or three minutes and the colour of the acid observed. Pure products do not colour the acid at all, and commercial products colour it pale yellow or brown according to the extent to which refining has been carried. The coloration may be measured by comparison with solutions of potassium dichromate in sulphuric acid.

(*b*) WITH BROMINE. 5 c.c. of the benzole are mixed in a beaker with 10 c.c. of dilute sulphuric acid (1 : 5) and a decinormal potassium bromide and bromate solution (9·9167 grams KBr + 2·7833 grams $KBrO_3$ per litre) run in, slowly and with shaking, at intervals of five minutes until the bromine liberated no longer undergoes absorption; this is shown by the orange-yellow coloration of the benzole and by the blue colour imparted to starch-iodide paper. The degree of refining is in inverse ratio to the amount of bromine absorbed (1 c.c. N/10-solution = 0·008 gram Br). The loss during further refining will be 1% per 0·2 c.c. of the bromine solution used.

⁂

The benzoles most commonly found on the market may come from the distillation of light tar oils or from the distillation of the washing oils obtained by exhaustion of the gas from the manufacture of coke or coal gas by means of heavy oils. These are mixtures in varying proportions of benzene and higher homologues. Examples of the more important characters of these products

TABLE XL

## haracter and Composition of Benzoles

| | Specific Gravity at 15° C. | Percentage of Distillate at different temperatures. | Composition. | | | |
|---|---|---|---|---|---|---|
| | | | Benzole. | Toluole. | Xyloles. | Higher homologues. |
| . . | 0·880–0·883 | 90–93% up to 100° | 84 | 13 | 3 | — |
| . . | 0·875–0·877 | 50–53% up to 100°<br>90–93% up to 120° | 43 | 46 | 11 | — |
| . . | 0·870–0·872 | 90% at 100–120° | 15 | 75 | 10 | — |
| . . | 0·872–0·876 | 90% at 120–145° | — | 25 | 70 | 5 |
| a) . | 0·874–0·880 | 90% at 130–160° | — | 5 | 70 | 25 |
| . | 0·890–0·910 | 90% at 145–175° | — | — | 35 | 65 |
| . | 0·920–0·945 | 90% at 160–190° | — | — | 5 | 95 |

s contain varying proportions of impurities. Thus, thiophene in the earlier of the above marks and carbon disulphide occurs 2–1% in benzole I and 0–0·5% in benzole II, whilst it is usually eding marks. In marks I, II and III, the amount of paraffin t most 1%, and in other marks rather more. Pure benzoles ·1 c.c. of the bromide-bromate solution, but the commercial 0·6–1%.

behaviour of the principal commercial products on fractional rectifier for the separation of the individual hydrocarbons e following serve as examples :

| | Benzole I. | Benzole II. | Pure commercial Benzole. | Commercial Toluole. | Commercial Xylole. |
|---|---|---|---|---|---|
| . . | 1·0% | 0·3% | 0·5% | 0·3% | 1·3% |
| . . | 78·8% | 18·3% | 98·0% | | |
| tion . . | 10·0% | 47·5% | 1·5% | | |
| . . | 8·0% | 23·7% | | 97·3% | |
| . . | 2·2% | 10·2% | | 2·4% | 96·5% |
| s, etc. . | | | | | 2·2% |

s of the three isomerides in commercial xylole are about *p*- and 5 of *o*-xylene.

## NAPHTHALENE

cating approximately the melting point. The fused mass is then stirred with the same thermometer until naphthalene crystals again begin to form and the column of the thermometer remains stationary for some time. This is the solidifying point, which, with pure naphthalene, corresponds with the melting point.

**2. Presence of Oily Products.**—A packet of 50 grams of the naphthalene wrapped in several thicknesses of filter-paper is subjected in a press to a pressure of about 150 atmos. for 10 minutes, the paper being then examined to see if it is stained by the oil absorbed.

**3. Behaviour towards Petroleum Ether.**—2 grams of the naphthalene are treated in a test-tube with light petroleum to see if a clear, colourless solution is obtained.

**4. Behaviour towards Sulphuric Acid.**—4 grams are heated in a test-tube in a water-bath with 4 grams of conc. sulphuric acid until a clear solution is obtained, the colour being observed. The sulphuric acid solution is poured into about 40 c.c. of water to ascertain if the whole remains clear and colourless.

**5. Stability towards Light.**—2 grams of the naphthalene on a clock-glass are left for 1–2 hours in a desiccator over conc. nitric acid (not fuming), the naphthalene being then examined to see if it has remained unaltered or if it is coloured.

⁂

*Pure* commercial naphthalene is white or slightly yellow and melts at 79·6–79·8°; it should not mark paper (test 2) and should volatilise completely if heated on a water-bath; test 3 should yield a clear solution, at most pink or reddish, which should remain clear on dilution; it should dissolve completely in petroleum ether (test 4) and should remain unchanged when subjected to test 5 (slightly impure naphthalene becomes pale pink).

## ANTHRACENE

Commercial anthracene is always impure, containing principally naphthalene, methylanthracene, carbazole, paraffin wax, phenanthrene, etc. The technical examination of crude anthracene is limited to the determination of the anthracene content and to tests for the presence of impurities which are harmful in the coal-tar colour industry.

**1. Determination of the Anthracene.**—Luck's method, based on the oxidation of anthracene to anthraquinone by means of chromic acid, is usually employed. In a flask with a capacity of about half a litre, fitted with a tapped funnel and a reflux condenser, a boiling solution of 1 gram of the anthracene in 5 c.c. of glacial acetic acid is treated with a solution ition and finally with boiling water until the alkalinity contents of the filter are washed by means of a fine water orcelain dish, the water being evaporated and the residue heated for 10 minutes on a boiling water-bath with 10 phuric acid (D 1·88). The dish is subsequently left in a hours, the contents diluted with 200 c.c. of cold water, e anthraquinone filtered, washed as before, placed in a ated, dried at 100° and weighed. For greater exactness is evaporated and the residual ash determined: anthra- = anthracene.

**of Impurities.**—Among the more common impurities l in certain applications of crude anthracene, e.g., in the izarin, are methylanthracene, carbazole, paraffin wax e. These substances are detected as described in the phs; for their quantitative determination, which is rarely and for special purposes, special works must be

THRACENE. When anthracene containing methylanthra- y chromic acid, as described above, methylanthraquinone forming threads variously twisted rather than needles e. Methylanthraquinone is distinguished from the latter solubility in benzene.

. The anthracene is extracted with ethyl acetate, the ed, and the residue treated with a few drops of ethyl re added some drops of nitrobenzene and a little phenan- he presence of carbazole is shown by the formation of nellar, copper-coloured crystals.

WAX. 10 grams of anthracene are treated with 100 c.c. ereal solution separated and evaporated and the residue grams of fuming sulphuric acid (20% of anhydride) for 0°. The whole is poured into 500 c.c. of water and, after fin wax separated at the surface is filtered off, washed he filter allowed to dry and then moistened with alcohol, collected by adding ether. The ethereal solution thus ated, and the residue, dried at 105°, gives the solid paraffin

RENE. A certain quantity (1 kilo) of the product to be d in the hot with double its volume of toluene. After allised anthracene and carbazole are separated and the illed, the portion passing over between 300° and 340°— he greater part of the phenanthrene being collected scales with an odour resembling that of naphthalene; according to the degree of purification, it contains 30–39% of anthracene (English anthracene A contains 40–50%).

*Pure anthracene* forms white, tabular crystals with a blue fluorescence, m.pt. 216·5°, b.pt. 360°; it is slightly soluble in alcohol, ether, benzine, carbon disulphide and cold benzene, and readily soluble in the hot in benzene, pyridine and glacial acetic acid.

## CARBOLIC ACID

*Crude* and *pure* carbolic acid are on the market. The former is of somewhat variable composition, the name being often given to yellowish or dark brown carbolic oils containing, besides varying quantities of neutral tar oils, also phenol and its homologues (mainly cresols), whereas it is also used to designate pale red products rich in phenols and crystallising more or less easily when cooled. The pure product is colourless or pale red, crystallisable and soluble in 15 parts of water.

In very impure products the determination of the phenols and neutral oils is carried out as in 2; in the others, the water, solidification point, and the solubility are determined (3, 4 and 5) and, if required, the quantitative estimation according to Koppeschaar (*see* 2).

**1. Characteristic Reactions of the Phenols.**—The following reactions are used:

(*a*) The aqueous solution of a phenol gives a violet coloration with dilute ferric chloride solution (provided mineral and organic acids, alcohol, ether and glycerine are absent).

(*b*) When heated gently with a little ammonia and a few drops of sodium hypochlorite, the aqueous solution of a phenol gives an intensely blue coloration.

(*c*) The substance is shaken with water and the aqueous solution treated with bromine water: if it is a phenol, a voluminous, white precipitate of tribromophenol, at first flocculent and afterwards crystalline, is produced. It is soluble in alkali and is reprecipitated on acidification of the alkaline solution. The tribromophenol reaction (*Landolt's reaction*) is sensitive to about 1 part in 44,000. The cresols and also other organic compounds are precipitated by bromine water.

(*d*) A very sensitive reaction is as follows: About 1 c.c. of the oil to be examined is shaken with 1 c.c. of alcohol, after which 2 c.c. of water and 1 c.c. of about 1% nitrazole solution (fresh) are added and again shaken: addition of a little caustic potash then colours the aqueous layer an intense red in presence of phenols.

**2. Determination of Phenols and Neutral Oils.**—The approxim

nt to dilute the sample with an equal volume of ligroin, t
ter being then subtracted from that of the neutral oils s
ontrol, the alkaline layer may be separated, acidified in a
and the volume of the phenols separating read.

exact results are obtained as follows: 120 grams of th
e examined are distilled until only about 8 grams of resid
sk, the distillate being dissolved in ether and shaken
rating funnel with 10% caustic soda solution. The tota
washed several times with ether and then acidified wi
cid diluted with an equal volume of water, the acid li
being extracted repeatedly with ether in a separating
the phenols. The ethereal solution of the latter is wa
d placed in a weighed flask, almost all the ether being dis
is then closed by a stopper through which passes a ver
a thermometer, and the last portions of ether then ev
g taken that the temperature does not exceed 100°; the
e-weighed, the increase in weight representing the phen
the phenol is *not accompanied* by its homologues (cre
e determined volumetrically by Seubert and Beckurts' me
eschaar's method:

s made of a solution of potassium bromide and brom
s, $5KBr + KBrO_3$, which in presence of an acid liberate
to the equation: $5KBr + KBrO_3 + 6HCl = 6KCl$
About 1 gram of the sample (or more, if poor in phenol)
lved in water to a litre, 25 c.c. of this solution being

while stirred with the thermo
the solidifying point of pure
mass beginning to crystallise
stationary. The highest t
point of the product tested

**5. Solubility.**—1 c.c. o
with 15 c.c. of water, should
pure. The more impurities

Pure carbolic acid has the
point, 183–184°. Products ar
to 32°), this resulting from t
cresols.

This is obtained mainly
crude or pure. *Crude pyrid*
of the pyridine and quinolin
bases, pyrrole and ammoni
penetrating and peculiarly
mable, soluble in water. *I*
proportions with water or
state it is used mainly for th
The following are the tests

**1. Colour.**—The colour

ermometer with its bulb central. The flask is heated over the
an asbestos card in such a manner that 5 c.c. distil per minute;
temperature reaches 140°, the heating is interrupted, the liquid
s over being still collected and the
the distillate measured. The distilla-
en continued up to 160° and the
the distillate measured.

**aviour towards Water.**—50 c.c. of
ne are treated with 100 c.c. of water
n if the two liquids mix completely
solution is clear or more or less
. The opacity may be determined
oking through the mixture in a tube
is indicated under 1 (above) and
g the possibility or otherwise of
int of definite dimensions.

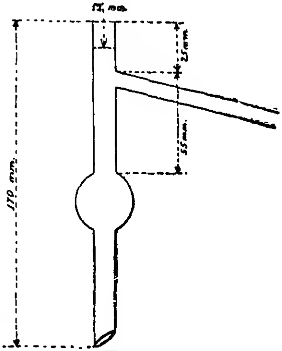


FIG. 39.

**aviour towards Caustic Soda.**—In a graduated cylinder with
stopper, 20 c.c. of the pyridine are shaken with 20 c.c. of caustic
on, D 1·4 (50 grams of sodium hydroxide in 100 c.c.) and left
r; the volume of the upper layer, consisting of the pyridine bases,
ad. The difference between this volume and 20 c.c. gives the
ent.

**ermination of the Bases.**—10 c.c. of the pyridine are diluted
to 100 c.c. and 10 c.c. of this solution titrated with normal sul-
d until a drop of the liquid produces on Congo red paper[1] a blue
h quickly disappears. The result is expressed by indicating the
c.c. of normal acid employed.

e exact determination is obtained by François' gravimetric
ased on the insolubility in anhydrous ether of the additive com-
pyridine hydrochloride with gold chloride. About 0·1 gram of
al is weighed into a porcelain basin and treated with water, 20–30
ydrochloric acid and excess of gold chloride solution, a precipitate
ed and the liquid remaining deep yellow. The whole is evaporated
on a water-bath and, when all the hydrochloric acid is eliminated,
decantation with anhydrous ether as long as any colour is still
to eliminate the excess of gold chloride). The precipitate remain-
dish is calcined and the metallic gold weighed: Au × 0·401 =
when pure pyridine is taken. With crude pyridine, the weight

Test 6 : the layer of pyridine [illegible] should occupy at least

Test 7 : not less than 9·5 c.c. N-sulphuric acid should be used.

## CHAPTER VIII

# MINERAL OILS

## AND PRODUCTS DERIVED FROM THEM

*le petroleum* yields various industrial products which may be grouped
ollowing classes :

*ight oils* (gasoline and naphtha), b.pt. below 150° C.

*amp oil* or *kerosene*, principally the fractions boiling between 150°
°.

*edium oils* (gas oils), intermediate to lamp oil and the heavy oils.

*eavy oils*, which include the fractions distilling above 300–310°
ated to render them suitable as lubricants.

*esiduum*, which consists of the residue left after distillation of the
d medium oils and sometimes also of part of the heavy oils, without
treatment.

*aseline*, composed of hydrocarbons semi-solid at the ordinary tem-
e.

*olid paraffin* or *paraffin wax*, formed of solid hydrocarbons.

lucts analogous to these are obtained by distillation of *bituminous*
nd are termed *shale oils* ; these also yield *light oils* (shale spirit),
*oils*, *heavy oils*, and a considerable quantity of solid paraffin.

ilar to the last is *ceresine*, obtained by refining *ozokerite* or *earth*
product of similar appearance to ozokerite is *montan wax*.

se products are treated in the following articles, together with *lubri-*
w largely used industrially and mostly having a basis of mineral oil.

ampling these products, reference may be made to the directions
or tar.

## CRUDE PETROLEUM

s is usually a brown or blackish liquid, but sometimes reddish or
with a characteristic bituminous odour ; it is often turbid owing

should be made at 15° or referred to 15°, the mean temper
of specific gravity being 0·0007 (0·0006–0·0008) per 1°.

**2. Fractional Distillation.**—In order that concorda
be obtained, this should always be carried out under certa
ditions and in an apparatus of fixed dimensions. Engler
in Fig. 40, is generally used. 100 c.c. of the oil are place
which is connected with a condenser 60 cm. long and heated
and the flask being protected with a sheet metal mantle.

The initial temperature of distillation is that at whicl
of distillate issues from the condenser fitted to the side-tu
The velocity of distillation should be such that two drop
second. The distillate is collected in several graduated cy
single 100 c.c. cylinder in which the volumes of the distillates

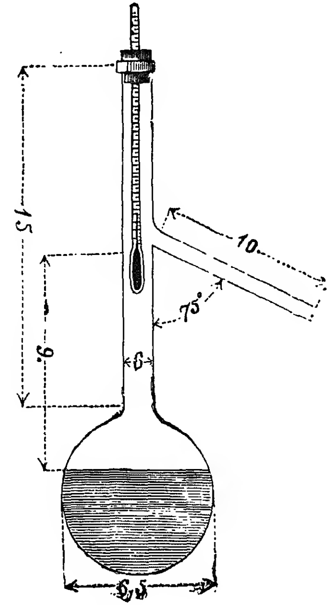
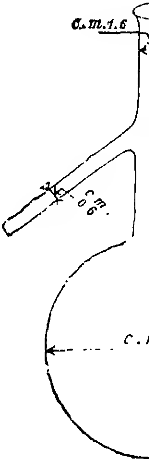


FIG. 40



FIG

temperatures are read off successively. The distillation is
the flask contains only residuum or white fumes appear.
usually collected are :

Benzine : up to 150° C.
Lamp oil : 150–300°.
Heavy oils : above 300°.

eight of the distillate up to 310° is determined.

the mineral oil contains much water, it is convenient to dehydrate neans of calcium chloride and to decant it before distillation in order id bumping during the heating.

**Flash Point.**—The *flash point* of an oil is the temperature correspondth the initial evolution of vapour forming with air a mixture capable loding in contact with a flame, or, more accurately, the temperature ich such vapour can be detected under definite experimental cons.

is determination is made with crude petroleum as with light oils (*see* With crude petroleums poor in light oils, however, the high flash equires the use of the apparatus employed with lamp oil or heavy *e* the paragraphs concerned).

**Temperature of Ignition.**—This is the temperature at which the l oil, coming into contact with a flame, ignites and continues to burn. determination, *see* Light Mineral Oils.

**Calorific Power.**—As a rule this is determined only when the crude eum is to be used as a fuel, as is the case with that from certain localities s, California); the Mahler bomb calorimeter is used (*see* Fuels). If troleum is poor in light oils, 1–1·5 gram of it is weighed directly into psule for holding the fuel, but if rich in volatile matter it is well to it in a small glass bulb with the ends drawn out, the igniting wire assed through the bulb; the bulb is placed in the capsule and just the bomb is closed the two ends are broken in order to facilitate of the oxygen to the liquid.

## 2. Chemical Tests

**Determination of the Water** (Marcusson's method).[1]—100 c.c. product are mixed with 50 c.c. of xylene and the mixture distilled, sence of a few scraps of pumice, best in an oil-bath until the water over. The distillate is collected in a graduated cylinder and the e of the lower aqueous layer measured.

**Determination of the Suspended Solid Matter.**—The oil is n with at least 20 times its volume of benzene (to dissolve any sus- d pitch and asphalt), filtered after standing for some hours, and sidue on the filter washed with benzene, dried and weighed.

**Determination of the Sulphur.**—This may be carried out by a's method (*see* Fuel) or in the Mahler calorimetric bomb. With 's method, 1 gram of the mineral oil is mixed with sufficient of the re of magnesia nd sodium potassium carbonate to give a dry powder.

acid precipitated as barium sulphate: $BaSO_4 \times 0{\cdot}1374 = S$.
This method is also applicable to all derivatives of crude p
always gives good results.

**4. Determination of the Solid Paraffin.**—This is effecte
method, after fractions below 300° have been eliminated.
100 grams of the crude petroleum are rapidly distilled, the dis
300° being collected. If the residue from the distillation is dar
as is usually the case, it also should be distilled—the therr
condenser having been removed—until only fixed, carbonac
remains in the retort. The distillate above 300° (or the oil
the flask if it is not distilled) is weighed and treated as follows i
tus shown in Fig. 42.

This consists of a vessel surrounded by felt and containi
mixture in which are immersed the tube
the test material and the funnel used for t
the funnel is connected with a pump flas
paratus is provided with another tube (5)
which the water from the freezing mixt
run off.

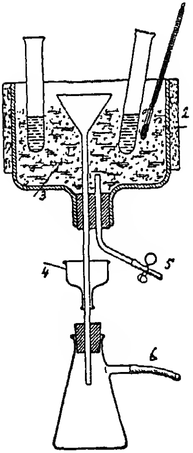


Fig. 42

Of the oil distilled as described above
are placed in a wide test-tube and diss
necessary quantity of a mixture in equa
of absolute alcohol and ether. The tube is
freezing mixture so as to keep it at abou
while the liquid is stirred with the therr
alcohol-ether mixture added until the oily
separate are redissolved and only the s
remains out of solution. The liquid is the
means of a pump on the funnel kept be
and −20°, the residue being washed
alcohol-ether mixture (if the solid paraffin is soft, it is well
a mixture of 2 parts of alcohol and one of ether) until a few c.c. o
liquid leave no appreciable oily residue on evaporation. T
solid paraffin is then dissolved on the filter in hot benzene into
dish, the benzene being evaporated on a water-bath—which
boil vigorously—and the dish dried for 15 minutes at 105°
desiccator and weighed. The percentage of solid paraffin in
oil is then calculated.

By this method, a small quantity of solid paraffin remains
the alcohol-ether mixture; the result obtained should, therefore

in a test-tube with 20 c.c. of petroleum ether (D not above 0·7) and left overnight; any hard asphalt present is deposited in blackish flocks soluble in benzene.

(b) *Soft asphalt.* About 0·5 gram of the oil is dissolved in a test-tube in 15 c.c. of ether and the liquid treated with 7·5 c.c. of 96% alcohol; any soft asphalt present is precipitated in the form of flocks, which unite to a viscous mass adherent to the walls of the tube and soluble in benzene.

2. QUANTITATIVE DETERMINATION. (a) *Hard asphalt.* About 5 grams (or more, with a product poor in asphalt) of the oil are shaken in a litre flask with 200 c.c. of the petroleum ether used for the qualitative test and left at rest for a day. The liquid is then decanted on to a pleated filter, to which also the insoluble substances are transferred, flask and filter being washed with benzine until a few drops of the filtrate leave no oily residue on evaporation. The insoluble residue on the filter is at once dissolved in hot benzene, the solvent evaporated in a tared dish and the residue dried at 105° and, when cold, weighed.

(b) *Soft asphalt.* 5 grams of the product are dissolved, in a bottle fitted with a ground stopper and of about 300 c.c. capacity, in 25 volumes of ether, 12·5 volumes of 96% alcohol being run in to the solution, drop by drop and with shaking, from a burette. After standing for 5 hours at 15°, the liquid is filtered and the bottle and filter washed with the alcohol-ether mixture (1 : 2) until the washing liquid leaves no oily residue, or at most traces of pitchy substances, on evaporation.

The precipitate, which may contain solid paraffin as well as asphalt, is dissolved in benzene, the solution evaporated, the residue treated repeatedly in the hot with 96% alcohol (about 30 c.c.) until the alcoholic extracts no longer deposit solid paraffin on cooling. The residue, consisting only of the soft asphalt, is dried for 15 minutes at 105° and weighed.

For precipitating the asphalt in mineral oils, besides benzine and alcohol-ether, also butanone,[1] amyl alcohol and ethyl acetate have been proposed.

Different solvents precipitate asphaltic substances in different quantities and of different qualities, so that the analytical results are only relative and not absolute.

**6. Behaviour towards Concentrated Sulphuric Acid.**—Concentrated sulphuric acid precipitates from crude petroleum asphaltic and pitchy substances in larger or smaller quantity. In many cases it is, therefore, useful to determine these substances, this being done in the following manner.

In a graduated cylinder with a ground stopper 20 c.c. of the oil are dissolved in 80 c.c. of petroleum ether (D 0·700, and ascertained by preliminary trial to be unattacked by conc. sulphuric acid), the solution obtained rich in middle fractions, and their heavy ones contain solid para petroleums are usually richer in light and middle than in heavy

The *flash point* is mostly near 0°, but varies with the content

The *sulphur* content is generally low (less than 1%), but in son in Texan and Californian petroleums, more is found (4–5%).

The *calorific power* of crude petroleums is as a rule 10,000–11, diminishes as the specific gravity increases. Petroleums poor i fractions are more particularly used directly as fuels, e.g., those o fornia and Mexico; petroleums with little sulphur are preferable pose, but those with larger proportions may also be used.

## LIGHT MINERAL OILS

### (Benzine)

These are volatile, mobile, colourless, or pale yellow liqu clear but sometimes opalescent, in which case the presence o be suspected.

The following tests and determinations are made:

**1. Determination of the Specific Gravity.**—This is by the methods indicated for crude petroleum.

For fiscal purposes the Italian Customs authorities use aerometers, one for the densities 0·610–0·700 and the other for By means of tables published on the authority of the Ministry density readings made at other temperatures are reduced to weight of any consignment is known, the volume can then b

Besides as a means of characterising the various products con the name light petroleum oils, the specific gravity may serve as of the presence of benzoles, oil of turpentine or light resin oils, all o much higher specific gravities—0·86 or more.

**2. Distillation.**—Use is made of the flask already describ petroleum, this being connected with a good condenser and sand-bath with a lamp the flame of which is completely enclos gauze cage, so that ignition of the vapours in case the flask be avoided.

The temperature at which the distillation commences is no distillate collected either in a graduated cylinder, the volume being observed, or in a separate tared vessel for each fractio being afterwards reweighed. If the whole of the liquid do over below 150°, the distillation is stopped at this temperat residue in the flask weighed.

a flask surmounted by a dephlegmator may be used.

With very light, rectified oils, it is useful to evaporate a portion on the water-bath to ascertain if any residue remains, or to allow a little to evaporate spontaneously on a filter-paper to see if any oily spot is left.

Where exact results are required, allowance must be made for the atmospheric pressure when this varies by as much as ± 5 mm. from the normal (760 mm.).

**3. Flash Point.**—For this purpose use is made of the inner vessel *A* of the Abel apparatus (*see* Lamp Oil, Physical Tests, 4), this being placed in a metal vessel about 6 cm. high and 9 cm. in diameter containing alcohol; this vessel, in its turn, is placed in a larger metal vessel, also containing alcohol and surrounded with felt. Solid carbon dioxide is introduced into the alcohol until the temperature in the liquid to be examined reaches —50° or —60°; the temperature is then allowed to rise slowly and the observations begun as with lamp oil.

This determination is seldom made, as it is known that naphtha has a low flash point, which is generally far below 0°, although with some of the heavier types it may be slightly above 0°.

**4. Temperature of Ignition.**—After the flash point has been determined, the cover of the vessel *A* is removed and for every 0·5° rise of temperature a flame is brought near to the surface of the liquid. The temperature of ignition is taken as that at which persistent combustion of the liquid itself takes place.

This determination also is rarely made for the reasons indicated above, the temperature of ignition being only a few degrees (3 or 4) above the flash point.

**5. Degree of Refining.**—The extent of rectification of a light oil is indicated by the following tests:

(*a*) The oil is shaken with an equal volume of conc. sulphuric acid to ascertain if the latter appears coloured after separation.

(*b*) The oil is shaken with boiling water and the latter subsequently tested with litmus and with barium chloride.

(*c*) The liquid is boiled for a few minutes with alcohol containing a few drops of ammonia and then treated with silver nitrate to see if any brown coloration develops.

**6. Detection and Determination of Benzoles.**

(1) DETECTION. (*a*) According to Holde, tar-pitch, previously washed with petroleum benzine (D 0·70–0·71) until the latter dissolves no more, is shaken with the light oil under examination. The latter becomes yellow or brown if tar benzoles are present.

Not less than 5–10% of benzoles are detectable in this way.

washed out with alcohol of the same con the cylinder and the volume made up to 100 c.c. and the v Any nitro-derivatives formed from benzoles present pass int the alcohol, while the mineral oil remains undissolved; if tl the latter has been diminished by 5 c.c., it is concluded that the benzoles.

This procedure is valid only for light oils composed of paraffin which are not attacked by nitric acid.

2. QUANTITATIVE DETERMINATION. This is effected by Böttcher's method, which is based on the absorption of aro carbons by sulphuric acid of D 1·84 at 15°, this being prep parts of conc. acid and 20 parts of fuming acid. In a flask l 75 c.c., surmounted by a long neck graduated in 0·1 c.c. for 5 of the oil are shaken for 15 minutes with 25 c.c. of the ab acid. After a rest of 30 minutes, concentrated sulphuric ac into the flask until the layer of benzine is entirely in the gra the volume of this being read off after the lapse of an hour. T between this volume and the original one represents the aro carbons.

**7. Oil of Turpentine.**—The procedure followed is that the detection of mineral oils in oil of turpentine (*see* Chapter o and its Products: Oil of Turpentine, 9, in Vol. II).

⁂

*Crude light oils* are usually yellowish and often contain a cer of less volatile oils, but the *rectified* products should be colourle give negative results with the tests described under 5 (above).

*Rectified light oils* are subdivided, according to the temperat they distil, into different products, named differently in vario Usually the following products are distinguished :

| Name. | | Specific Gravity. |
|---|---|---|
| Light petroleum ether (Gasoline I) | | 0·620–0·66 |
| Heavy petroleum ether (Gasoline II, Light benzine) | | 0·660–0·68 |
| Benzine for pleasure automobiles | Petrols | 0·680–0·70 |
| Benzine for ordinary automobiles | | 0·690–0·72 |
| Benzine for heavy automobiles | | 0·720–0·77 |
| Benzine properly so-called (Naphtha C) | | 0·670–0·72 |
| Ligroin (Naphtha B) | | 0·707–0·73 |
| Cleaning oil, Naphtha (Naphtha A) | | 0·720–0·75 |
| Substitute for oil of turpentine | | 0·730–0·75 |

# LIGHTING OIL

Paraffin oil or kerosene, used for lighting purposes, is a clear mobile liquid, sometimes colourless, but usually more or less yellow and fluorescent and of characteristic odour. Physical as well as chemical tests are made.

## 1. Physical Tests

**1. Colour.**—The colour of lamp oil may be used as a basis for commercial contracts. Its intensity is determined by Stammer's colorimeter (Fig. 43), which consists of two vertical brass cylinders blackened inside, one of them, closed at the bottom by a glass, being charged with the liquid to be examined; in the other cylinder is inserted a standard glass coloured with uranium oxide to a definite intensity, and under both cylinders is a white reflecting surface. By means of two prisms, the two colours to be compared are observed in the two halves of the circular field of the eyepiece. The depth of the liquid may be varied by vertical displacement of the system of prisms along with a cylinder closed at the bottom by a glass disc and dipping into the cylinder of liquid. When uniformity of the field has been attained the depth of the liquid giving a colour intensity equal to that of the standard glass is read off on a scale.

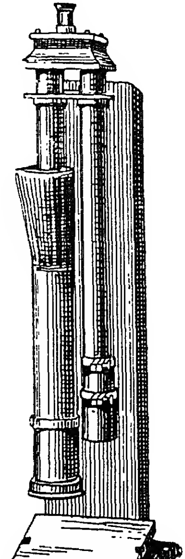


FIG. 43

The four grades of colour usually distinguished in the trade, with the corresponding depths in Stammer's colorimeter are:

| | |
|---|---|
| Standard white. . . . | 50 mm. |
| Prime white . . . . . | 86·5 ,, |
| Superfine white . . . | 199 ,, |
| Water white . . . . . | 310 ,, or more |

In England and Russia, use is largely made of the Wilson colorimeter,[1] which contains four standard coloured glasses corresponding with the different commercial grades.

**2. Determination of the Specific Gravity.**—As with crude petroleums, at 15°.

For determining the density of lamp oil for fiscal purposes, the Italian Customs authorities use a thermo-aerometer graduated from 0·750-0·840, and tables of temperature corre t o have been prepared.[2]

*l*. Its cover carries a thermometer *t* with a scale extending
50° and divided into half-degrees, and a clockwork mechani
motion by a lever *a*. Pressure of the latter opens automatic
window in the cover and at the same time lowers a small flam

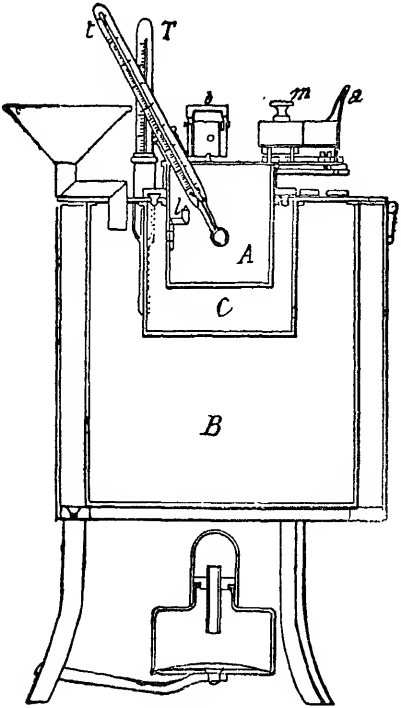


FIG. 44

aperture and then rais
the window immediat
The entire movement sh
two seconds.

The vessel *A* is heate
bath *B*, the intermedi
being left empty, and i
on an ebonite ring fixed
*B*. The latter contain
meter *T* with a red m
The bath is first hea
temperature, the covere
taining the oil up to th
level being fitted anc
mometer *t* in the oil reac
rise of temperature of 0·
work mechanism is o
test being repeated unt
causes a small explosion
perature then shown i
point and should be co
the pressure (± 0·035°
below or above 760 mm
being returned to the r
degree.

The dimensions of all parts of the apparatus are exactl
and with careful working the results should not vary by more
at the most.

**5. Temperature of Ignition.**—When the flash point
measured, the cover of the vessel *A* is removed and a therm
ported in the oil, the heating being continued and, after eac
flame brought near the surface of the liquid without touching
the oil fires, the temperature is observed, the thermometer i
withdrawn and the oil extinguished with an asbestos card.

**6. Determination of the Viscosity.**—This is not usually
with illuminating oil, but it may, if required, be effected as ir
(*q.v.*, Physical Tests, 7) or, ore exactly, by means of the

**Determination of the Illuminating Power.**—This requires a *eter*, one of those most largely used being that of Lummer and Brod- ig. 45), which is an improved form of the Bunsen type. It consists

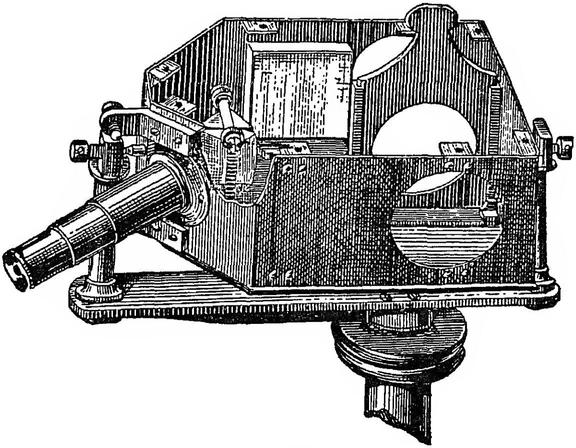


Fig. 45.

osed chamber with two opposite circular apertures, by means of he two faces of a white screen in the chamber are illuminated respec- y the lamp to be examined and by a lamp chosen as unit. The two f the screen reflect the light, by means of a system of lenses, on to centric zones of the field of the telescope ce shown to the left of the figure. When een is equally illuminated on both faces, the es of the field appear exactly similar. The rces of light are placed at the extremities of a guide 3 metres in length and graduated in timetres—the *photometric bench*. The position hotometer is adjusted between the lights so e field is uniformly illuminated: the inten- the two lights are then proportional to the of their respective distances from the screen

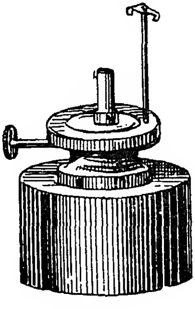


Fig. 46

TABLE XLI

| Unit. | Hefner Candle. | International Candle, Decimal Candle (Norma Candle), American Cand Pentane Candle. |
|---|---|---|
| Hefner candle . . . . . | I | 0·9 |
| International candle, decimal candle (normal candle, American candle, pentane candle . . . . . . . | 1·11 | 1 |
| Carcel . . . . . . . | 10·75 | 9·65 |

The petroleum to be tested is poured into a lamp and the centred on the photometric bench and lighted, the time bei flame is kept low at first and is then gradually raised until possible without smoking and without the wick charring exces metric observations are then begun and are repeated at re —the time of each being noted—until the oil is almost exha not being further moved; the lamp is finally extinguished the consumption of oil being thus ascertained.

The position of the Hefner lamp is taken as the zero o that of the oil lamp as 300 cm.; the illuminating power of t given by the formula,

$$i = \left(\frac{l - x}{x}\right)^2$$

where $i$ is the intensity required, expressed in candles length of the photometric bench and $x$ the distance of t screen from the zero point of the scale. The mean of the vations gives the mean intensity in candles.

The mean consumption per candle-hour is the quotien weight of oil used by the total candle-hours, and the yiel amount of light (in candle-hours) produced per gram of oi of the total candle-hours by the weight of oil consumed.

It is necessary also to take account of the variation o intensity during the experiment. As a rule, after reaching a few minutes subsequent to the lighting of the lamp, it di or less slowly to the end, mainly on account of the carbon

ng intensities were observed, the
ption of oil being 180 grams.

| Time. | Luminous intensity in candles. |
|---|---|
| 1st hour | 9·50 |
| 2nd ,, | 9·00 |
| 3rd ,, | 8·50 |
| 4th ,, | 8·00 |
| 5th ,, | 7·50 |
| Total candles | 42·50 |

n luminous intensity = 42·50 : 5 = 8·50 candles.
n consumption per candle-hour = 180 : 42·50 = 4·23 grams.
d, or light produced per gram of oil = 42·50 : 180 = 0·23 candle-hour.
ease of luminous intensity = (9·50–7·50) : 9·50 = 0·21.

ust be pointed out that petroleums of different quality do not burn well in all lamps, principally on account of the different quantities of require to burn completely. If the lamp does not allow access of t air the combustion, being incomplete, will give rise to smoke and ant smell, whereas excess of air in the flame will cool the latter too much inish the luminosity as well as the consumption. In general, Russian oils more air than the American, while with oils from the same locality, is required by those rich in heavy and poor in light fractions. In any s necessary, to obtain comparable results, to work with the same lamps allow for the form and dimensions of their essential parts, namely, the burner and chimney. Marked influence on the course of the combus-lso exercised by the wick, especially the length and quality of the fibre structure and compactness of the tissue; wicks of the same quality ensions should be used in all measurements, and they should be either washed thoroughly with petroleum ether and then dried.

**ehaviour at Low Temperature.**—This test is made on oils to in the open in cold places. A little of the oil is cooled for an hour, t-tube with a thermometer passing through its stopper, at the lowest ature to which it is likely the oil may be exposed, to ascertain if remains clear and mobile or if solid substances separate. For the re, *see* Heavy Oils, Physical Tests, 8.

## 2. Chemical Tests

**cidity.**—This may be due to inorganic acids (principally sulphuric to organic acids. The tests are made as follows:

NORGANIC ACIDS. The oil is shaken with tepid water containing methyl orange; if the colour changes to red, the aqueous layer is ed and tested with barium chloride.

If any appreciable coloration occurs, it is desirable to ascertai
rise of temperature takes place.

**3. Determination of the Sulphur.**—This is usually
oils having a penetrating and unpleasant odour. The sim
that of Heussler and Engler,[1] this consisting in burning th
a suitable lamp, the chimney of which is joined to a bent tu
20 c.c. of 5% potassium hydroxide solution made just yell
and then left in the air to decolorise; the absorption vesse
with a pump. The lamp charged with the oil is weighed a
tube fitted and the suction adjusted so that the combustion
regular. The sulphurous anhydride produced is absorbed a
into sulphuric acid by the alkaline bromine solution. Aft
of the oil are burnt, the flame is extinguished, a little more air
the lamp again weighed and the sulphuric acid determined
phate. The caustic potash used and also the air must, of
from sulphur products.

The sulphur may also be determined by the Mahler calorin
Crude Petroleum, Chemical Tests, 3).

**4. Distinction between Petroleums from Different**
This is based mainly on the following tests:

(*a*) SPECIFIC GRAVITY. This is usually 0·780–0·805 for
0·820–0·825 for Russian lighting oils.

A better criterion than the specific gravity is furnished by the
of the fractions obtained on distillation, these differing by about
boiling points. Thus, the fractions of an American and a Ru
distilling between 230° and 250° have the respective densities
and the fractions between 250° and 270° the densities 0·809 a

(*b*) TREATMENT WITH BROMINE. 2 or 3 c.c. of Amer
are not coloured when treated with a drop of bromine,
petroleums become coloured under these conditions.

(*c*) SOLUBILITY IN A MIXTURE OF CHLOROFORM AND A
and Halphen [2] have suggested a method based on the differe
in a mixture of chloroform and aqueous alcohol, of fractions
gravities from American and Russian petroleums. It is
follows: Several successive fractions of the oil are separate
and the specific gravity of each of them determined at 15
of a mixture in equal volumes of pure anhydrous chlorofo
alcohol necessary, when run in slowly from a burette with co
to remove the turbidity produced, is then determined.
fractions (which have about the same compositions wit

* *

*d lamp oil* should be clear and only slightly coloured (in time, however, g occurs if the oil is exposed to the air); its odour should be neither trating nor unpleasant, as this would indicate the presence of sulphur ıds.[1] It should have no appreciable acidity and should not turn brown phuric acid. For use in cold places, it should remain clear and mobile nperature lower than that to which it is likely to be exposed. The ravity is usually 0·780–0·805 for American and 0·0820–0·825 for Russian

regard to *fractional distillation*, a good oil should not begin to distil o° and should contain only small amounts of light and heavy oils. The sually demanded for ordinary lamp oils are 5% of light oils and 10% oils, but the proportions actually present are well within these limits l oils. As regards the fractions comprised between 150° and 300°, ould be no great disproportion between the amounts of these and the ractions should predominate over the extreme.

*flash point* is of importance as an indication of the danger attending of the oil. In Italy, legislation demands that the flash point for lamp rmined by the Abel-Pensky apparatus, should not be below 21° C.

*viscosity* of lamp oil, measured by the Engler apparatus at 20° C., is or, measured by the Ubbelohde apparatus, 1·10–1·80, and is usually at lower for Russian than for American oils.

*illuminating power* varies with the lamp used, but, under ordinary con- the consumption per candle-hour at 15–20° varies from 3·5 to 5 grams. rease in luminosity from the beginning to the end of the combustion ally greater with American than with Russian petroleums. The latter th a less initial and greater final luminosity than the former. In any h a good oil the decrease should not exceed one-fourth of the initial

oils from crude petroleums rich in solid paraffin, e.g., those from v, Pennsylvania, etc., if not properly prepared, deposit *solid paraffin* °, but those of Russian origin remain clear even at − 20°.

*calorific power* of lighting oil is 11,000–12,000 cals.

## MIDDLE OILS

## (Gas Oils)

se are intermediate in character to lighting oil and heavy oils. They bile and yellow to dark brownish-yellow, their density being between ·845–0·855, their b.pt. 300–350°, and their viscosity below 3 (Engler). most important determination with these oils is the yield of gas calorific value of the latter. The amount of gas given is determined hall works plant. In the laboratory it may be ascertained approxi- in comparison with a typical oil, in Ross and Leather's apparatus,[2]

---

cording to Kissling and Engler (*Chem. Rev. Fett. Ind.*, 1906, p. 158), the pro-

consisting of a retort (23 × 14·5 × 12 cm.) in which 15 c.c
gasified. The temperature of gasification is measured wit
and the volume of gas produced and the components absorba
sulphuric acid determined.

Another apparatus for this purpose has been proposed
and modified by Hempel.[1] The results obtained on the la
are, however, not accurate, the best method being the wo

The following determinations may also be required : Sp
behaviour on distillation, flash point, viscosity, calorific powe
these being carried out as indicated in the articles dealing with
and *heavy oils*.

*Middle* or *gas oils* are used for making illuminating gas,
water gas, as a motive force, as a cleaning oil, and also as solve

The yields from 1 kilo of oil vary between the following limit
litres ; tar, 300–400 grams ; coke, 40–60 grams.

## HEAVY OILS

## (Lubricating Oils)

These oils vary somewhat in colour, appearance and con
colour is usually reddish, brown or blackish, and marked
also observed ; some such oils are, however, colourless or
not at all or but slightly fluorescent (vascline oil). The s
to that of lamp oil if more volatile oils are present, but very
odourless. A bituminous smell indicates faulty refining a
resinous odour the presence of extraneous matter. As a
are liquid and more or less viscous, but some are highly mo
have almost the consistency of fats.

Analysis of lubricating oils aims at ascertaining if their
in correspondence with the uses for which they are design
conditions fixed in the purchase contract.

Both physical and chemical tests are made.

### 1. Physical Tests

**1. Colour.**—This is usually compared with that of a
means of the colorimeter (*see* Lighting Oil) or more simply
equally thick layers of the two oils in similar rectangular

**istillation.**—The flasks used for crude petroleum are employed. nperature at which the distillation commences is noted and the up to 300-310°, representing the light oils and illuminating oil, and weighed.

scal purposes (in Italy), the procedure followed is that indicated under *troleum*, 2. When decomposition occurs, recourse is had to distillation duced pressure, as indicated later for residues.

**olatility.**—When heated, heavy oils begin to emit vapour at a point. To determine the quantities of the oil evaporating in a ime at different temperatures, in accordance with the conditions vn in contracts, the following procedure (Holde) is employed: container *A* of the Pensky-Martens apparatus (Fig. 47) is charged to k with the oil and weighed. It is then heated for the prescribed or temperatures between 100° and 200°, a glycerine bath is used, higher temperatures (200–300°) a bath of a heavy cylinder oil flash point above 300° is employed.

emperature of the oil is measured by means of a thermometer from e adhering oil is removed by a piece of filter-paper (previously with the crucible), which is added to the oil. After the experiment, ontained is cooled in water, dried, left in a desiccator for about 30 and weighed; the loss in weight gives the volatile oil.

temperatures higher than 300°, the oil may be heated directly ensky-Martens apparatus.

**lash Point.**—This is determined for heavy oils in the Pensky- apparatus (Fig. 47). The upper view shows a section of the essens of the apparatus. *A* is a brass cylinder similar to that of the paratus and is fitted with a level gauge and a vaned stirrer *a*; it l inside an iron envelope *B* with very thick walls. This part of aratus is surrounded and protected from radiation by a cupola- brass mantle and is heated by means of a triple burner *C*, a wire being interposed. The cover of the vessel *A* carries a thermometer graduated from about 80° to 250°, with its bulb dipping into the nd a gas flame *f* which is brought near to a small window and the the same time opened by turning a knob *b*. A fixed flame *l* serves nt the movable flame when this is extinguished by the explosion. imensions of the apparatus are fixed exactly.

oil (previously dehydrated with calcium chloride if it contains s placed in the vessel *A* and the apparatus heated to 80°, after ne stirrer is started and the flame regulated so that the temperature ut 5° per minute. Observations are made firstly at intervals of ture rises about 5° per minute, a small flame being brought of the crucible at regular intervals until a slight explosion

The results obtained by these two different methods vary i composition by 5–40°; the method employed for the determ always be indicated.

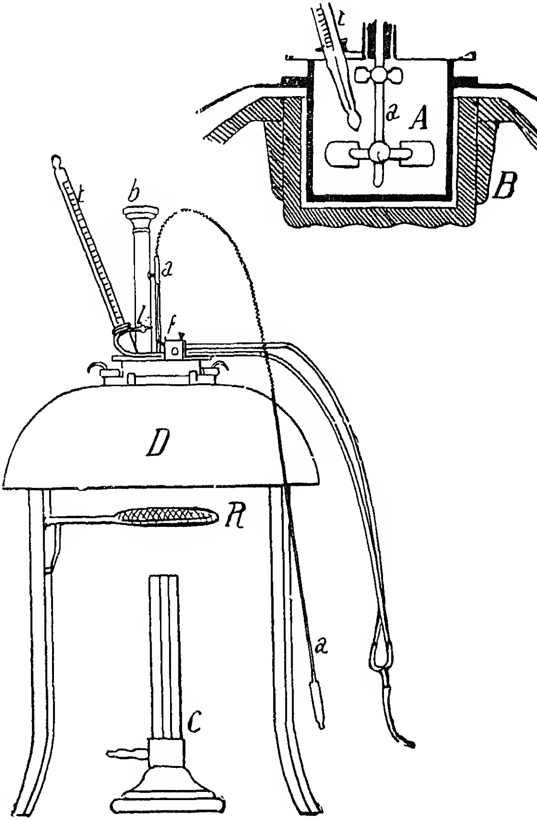


Fig. 47

**6. Temperature of Ignition.**—This determination ma the complement of that of the flash point—when an open cruci —by continuing to heat so that the temperature rises fro minute; a flame is held for 1–2 seconds near the surface of temperature of ignition being taken as that at which the su ignites.

The temperature of ignition is usually 20–60° above the fla

the temperature constant. Ther-
eters *c* and *d* give the temperatures in the vessel *A* and in the bath, he latter is heated by means of a ring burner ; the whole is supported tripod. Under the efflux tube is a glass flask *C* with marks on the at 200 c.c. and 240 c.c. All arts of the apparatus are of *y* standardised form and dimen- .

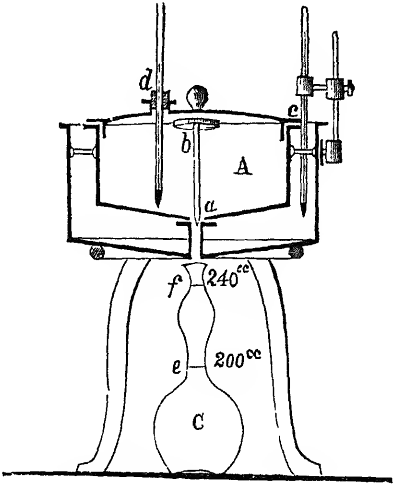


FIG. 48

o make a determination, the nal vessel is filled to the desired with the oil to be examined drated by decantation and ed through cotton wool dried 00°), the efflux orifice being The outer vessel is then filled water and heated carefully the oil reaches the temperature hich the viscosity is to be ured. The flask is then placed neath and the plug rapidly drawn, the time being counted ly from this instant. The time taken to fill the flask to the 200 c.c. mark, divided by that under similar conditions, with a standard liquid, gives the viscosity e oil in Engler degrees.

sually a temperature of 20° is employed and water taken as the standard, he apparatus should be controlled from time to time with water ; as e 52–53 seconds are required for the efflux of 200 c.c. of water.

etween one determination and another of the time of efflux of water, the ence is ± 1·5 second, which corresponds with a difference of ± 3% in egrees Engler. If, then, the difference in the time of efflux of water is han 1 sec., as prescribed for the use of the apparatus, the difference in the es Engler is ± 2·3%.

ach apparatus is sold duly controlled, the time of efflux for water being ated.

or very dense heavy oils, and for such semi-solid products as vaseline, iscosity should be determined at a higher temperature, e.g., 50°, 60°, or, sometimes, 180° or even higher. In the latter cases the whole e apparatus is placed in a large oven, or use made of an apparatus in h the outer vessel—tightly closed and fitted with a reflux condenser

*lubricating value*; the latter may be determined directly by
machines, that of Martens[1] being most commonly employed

Viscometers of other types are those of Lamansky-Nobel[2] (
wood[3] (Great Britain) and Saybolt[4] (America). In France us
Barbey's *ixomètre*, which determines the coefficient of fluidity of an
ing the volume of an oil dropping during a certain time.

The ratio between the values of the viscosity found by the La
and Engler apparatus respectively is about constant and is 1·13-
oils and 1·20–1·26 for more viscous oils (engine and cylinder oils), s
of Engler degrees = number of Lamansky-Nobel degrees divided b

The relations between Engler values and those obtained w
wood and Saybolt apparatus are given by the following formula
and $t_s$ represent the times of efflux in the two apparatus and $E$ the E

$$(1)\quad t_r = 192{\cdot}2k\left(1 + \sqrt{1 + \frac{0{\cdot}01624}{k^2}}\right)$$

$$(2)\quad t_s = 228{\cdot}7k\left(1 + \sqrt{1 + \frac{0{\cdot}01309}{k^2}}\right)$$

$$(3)\quad k = 0{\cdot}08019E - \frac{0{\cdot}07013}{E}$$

In practice, for viscosities which are not too low (not less than
Engler), it is a sufficiently close approximation to assume that
efflux in the Engler, Redwood and Saybolt forms of apparatus (u
to the conditions prescribed for each case) are in the ratios 100 :

**8. Behaviour at Low Temperature.**—When strongly c
cating oil first thickens and ultimately congeals and the aim of
its behaviour is either to ascertain if the oil remains liquid
temperature or to discover when it begins to thicken witho
a tallowy consistency.

In the former case a test-tube 15 mm. in diameter is fille
of about 3 cm. with the oil and placed, together with a ther
beaker about 12 cm. in height and diameter containing a sal
known freezing point[5] corresponding approximately with the
at which the oil should remain liquid. The whole is placed i
ware vessel and cooled for an hour with a freezing mixture
two parts of snow or pounded ice and one part of common salt
is then taken from the solution to see if the oil has remained l

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[1] D. Holde: *Untersuchung der Kohlenwasserstofföle und Fette*, Berlin,
W. Hinrichsen: *Das Materialprüfungswesen*, Stuttgart, 1912.

[2] Wischinsin and Singer: *Chem. Rev. Fette Industrie*, 1897.

[3] B. Redwood: *Petroleum*, London, 1913.

[4] B. Redwood: *Petroleum*, London, 1913.

[5] For this purpose the following solutions may be used:

| Freezing point. | Compositio |
|---|---|
| − 3° | Water, 100 : KNO |

in a test-tube through the stopper of which passes a thermometer, and cooled in a freezing mixture; from time to time the tube is withdrawn for an instant and inclined, so that the temperature at which the oil begins to solidify may be discovered. A saline solution with a freezing point a little lower than this temperature is then chosen and the oil kept in the apparatus referred to above at the temperature found in the preliminary trial. At the end of the time the test-tube is removed from the solution and inclined so that an idea may be obtained of the degree of thickening; the latter may also be estimated by noting the adhesion of the oil to a glass rod when this is withdrawn.

Supercooling of the salt solution is avoided by scraping the congealed parts from the walls of the containing vessel or by withdrawing the vessel itself for an instant from the freezing mixture.

If the cooled oil is heated and another examination made of the behaviour at low temperatures, the result may be different from that of the first test; such difference may be due to the variations of temperature to which the oil is subjected during transport and storage. It is therefore useful to carry out the test on the oil, first as received and then after it has been heated to 50° for ten minutes and subsequently cooled for 30 minutes in a water-bath at 20°. With mixtures of mineral and fatty oils, the cooling should be protracted for 4–10 hours, one test being made without stirring the oil and the other with stirring every 15 minutes.

**9. Test of Fluidity at Low Temperatures.**—This is effected when required by pipetting the oil into a U-tube of definite diameter (usually 6 mm.), cooling the latter in a cooling mixture, and then measuring the change of level produced by applying at one side, for a definite period (generally 1 minute), a known pressure, e.g., 50 mm. of water, by means of a water manometer. The number of mm. measuring the change of level represents the degree of fluidity of the oil at the temperature of the experiment.

## 2. Chemical Tests

**1. Detection of Water and Solid Substances.**—These are usually recognised by the appearance and are investigated as with crude petroleum. Water may also be detected by heating the oil in a test-tube for about 15 minutes: if water is present froth is formed and drops of water appear in the cold part of the tube.

**2. Determination of the Acidity.**—Acidity is due either to mineral acids (sulphuric acid) introduced during refining or to organic acids.

(*a*) Acidity due to mineral acids may be detected by shaking 50–100 grams of the oil with double the quantity of distilled water, allowing the aqueous layer to separate, filtering it through a moist filter-paper a d c.c. of absolute alcohol and 50 c.c. of the separated alcoholic lay with decinormal alcoholic caustic soda in presence of phenolph

The acidity is expressed as sulphuric anhydride or oleic acid number of milligrams of potassium hydroxide necessary to nc gram of the oil, the last being termed the *acidity number* of the $SO_3$ = 7·05% oleic acid = acidity number of 14.

**3. Alkalinity.**—This is detected by adding phenolphthalein aliquot part of the water with which the oil was shaken in the c tion of the mineral acids; with free alkali a red coloration is o

It must be borne in mind that, if the oil in question contains al the alkalinity found may be due to partial decomposition (hydroly soap by water.

**4. Determination of the Solid Paraffin and Asphalt.**—A petroleum (*q.v.*, Chemical Tests, 4 and 5).

**5. Detection of Oils, Fats and Waxes.**—(1) QUALITA c.c. of the mineral oil are heated for about 15 minutes in a test- a stick of caustic soda weighing about 4 grams, either over a na or, better, in a paraffin bath at 200–210°. If fatty substances ar even only to the extent of 1–2%, the whole mass becomes solid and on cooling.

(2) QUANTITATIVE. If the qualitative test gives a positive r quantitative estimation may be carried out as follows:

(*a*) By the saponification number determined as indicated substances; about 5 grams of substance are used and, besides potash, an equal quantity of benzene is added, the heating in a reflu tus being continued for about an hour. The saponification nur obtained is divided by 1·85, the result being the percentage of stances calculated from the mean value of their saponification r

In presence of wool fat or waxes—which are usually detectable by and consistency—the results obtained are inaccurate, since these have saponification numbers different from those of fatty substanc

(*b*) By direct weighing, according to the directions given b and Rodano[2]:

5 grams of the oil are saponified in a flask with alcohol solution (12 grams of caustic potash in 100 of alcohol), the fl immersed in a bath of boiling water. As reflux apparatus, a sim is placed in the mouth of the flask, so that a large part of the

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[1] According to H. Loebell (*Chem. Zeit.*, 1911, 35, p. 276), the acidity is

lost by evaporation ; sufficient, however, remains for the saponification, which takes place fairly rapidly (in about half an hour).

Without evaporating off all the alcohol, the contents of the flask are poured into a separator and the flask thoroughly rinsed out, at first with small quantities of alcohol and then with ether. Sufficient water is added to dissolve the soap formed and sufficient ether to dissolve the mineral oil. The alkaline liquid is almost neutralised towards phenolphthalein by means of acetic acid and shaken, a sharp division occurring on standing between the ethereal layer containing the mineral oil and the soap solution. The ethereal liquid is separated, washed with distilled water until the alkaline reaction disappears, and distilled from a tared flask, the last traces of ether being expelled in a current of air.

The residue is dried in an air-oven at 105° for an hour and weighed ; the weight is multiplied by 20 and the product subtracted from 100, the remainder being the percentage by weight of the fatty substance.

To determine the nature of the fatty matter, the soap solution is treated with dilute sulphuric acid and the fatty acids collected and identified by their colour reactions and their physical characters (*see* chapter on Fatty Substances). If blown or oxidised oils have been added to the mineral oil, the fatty acids are brown, have an odour of vegetable oils and are soluble in ether, from which they are partially precipitated by petroleum ether ; the precipitated part has a pitchy appearance. In some of their characters, these fatty acids might be confused with those of fish oils, but the latter have a quite different odour and are precipitated by Halphen's bromine reagent (*see* Fish Oils), with which the fatty acids of oxidised oils give no precipitate.

When it is necessary to examine the characters of mineral oil changed by previous operations, the saponification is carried out in the cold as follows :

In a separating funnel, 50 grams of the oil, 200 c.c. of light petroleum ether and 200 c.c. of 10% alcoholic potash (in 95% alcohol) are vigorously and frequently shaken for about four hours and then allowed to settle, the ethereal layer being separated and washed several times by shaking with cold water, and the petroleum ether evaporated on a water-bath. The residue consists of the mineral oil ; its freedom from fatty matter may be ascertained by determining its saponification number, which should be almost zero.

**6. Detection of Alkaline and Alkaline-Earthy Soaps.**—1. QUALITATIVE. The alkaline soaps may be dissolved by shaking the oil with water, whilst the alkaline-earthy soaps are decomposed by shaking with hydrochloric acid : in this way the bases pass into solution in the hydro-

**7. Resin Oils.**—1. DETECTION. Resin oils are detectec odour and by Morawski's reaction, which consists in treating a sm of the oil in a test-tube with acetic anhydride and adding a drop acid (D 1·53): the appearance of a transient violet coloration ir presence of resin oil.

Resin oils may be detected also by shaking the oil (freed, i from saponifiable matter) with an equal volume of acetone ar the two liquids to separate, the acetone containing very little and almost the whole of the resin oil. If the solvent is evap resin oil in the residue may be characterised by the red colora it imparts to an equal volume of sulphuric acid (D 1·6), by its h gravity (0·970–0·980) and by its rotatory power.

2. DETERMINATION. Storch's method is used: 10 grams (freed from saponifiable matters when these are present) are t flask, at a gentle heat and with shaking, with 50 grams of 96 After cooling, the alcoholic liquid is transferred to a weighed the oily liquid washed with a little alcohol, which is also added to The alcohol is evaporated on the water-bath and the residue w This residue is treated again with alcohol (10 times its weight), of the alcoholic solution giving a new residue (*B*). The mineral in this residue is calculated by means of the formula, $\frac{(A - B)}{(a - b)}$ and *B* are the weights of the two residues and *a* and *b* the q alcohol used in their treatment. Subtraction of the calculatec mineral oil from *B* gives the quantity of resin oil.

EXAMPLE: 10 grams of oil, treated with 50 grams of alcohol, ga of 1·51 gram (*A*), and this, treated with 15·1 grams of alcohol, gav 1·15 gram (*B*). From the proportion

$$50-15{\cdot}1 : 1{\cdot}51-1{\cdot}15 = 15{\cdot}1 : x,$$

$x = 0{\cdot}155$. Amount of resin oil in 10 grams of the oil taken = 1·15 0·995 gram.

**8. Tar Oils.**—The presence of tar oils is recognised besid characteristic odour, by the property they exhibit of reacting e with nitric acid (D 1·45) giving nitro-derivatives, by their s conc. sulphuric acid on a water-bath with formation of compou in water, and by the general reactions of the phenols (*see* Ta bolic Acid).

**9. Defluorescent and Odoriferous Substances.**—To c fluorescence of heavy oils, *α*-nitronaphthalene is usually empl lene is converted into α-naphthylamine, recognisable by its characteristic disgusting odour. The acid liquid is separated by means of a separating funnel, rendered alkaline with soda and extracted with ether, the ethereal solution being evaporated and the residue taken up in a little alcohol and treated with a drop of sodium nitrite solution acidified with acetic acid: the appearance of a yellow coloration changing to crimson indicates the presence of α-naphthylamine.

⁂

*Heavy mineral oils* have a specific gravity usually between 0·840 and 0·930, although occasionally the value 0·960 is attained. They should not contain any marked quantity of oils distilling below 300° and their flash point should not be below the specified limit laid down in relation to the purpose for which they are to be used. Usually this temperature is above, and often greatly above, 140°. Heavy oils are classified into numerous types having the following characters:

*Light oils for engines, gearing, motors and dynamos*, viscosity mostly 13–25 (at 20°) and flash point 180–220°.

*Spindle oil*, very fluid, viscosity 3·5–15 (at 20°), flash point 160–200°.

*Oils for compressors and refrigerating machines*, still more fluid than the preceding, viscosity 5–7 (at 20°), flash point 140–180°; the solidification point should be below – 20°.

*Automobile oils* (*cylinder*), viscosity varying according to the season from 20 to 85 (at 20°), flash point 185–215°.

*Pale heavy oils for engines and gearing*, viscosity 25–45 or more (at 20°) flash point 190–220°.

*Dark heavy oils for locomotives and railway wagons*, viscosity 25–60 (at 20°) and consistency varying with the season.

*Cylinder oils for steam engines*, boiling point high, very viscous (23–60 at 50°), moderately thick, flash point 240–315°, or, for some qualities, 350° or higher. These oils are divided further into low and high pressure cylinder oils.

Another type of heavy oil is that used for electric *transformers*. This should not contain water or mineral acids (reaction neutral) and should be non-volatile; when heated at 100° for some hours it should not decompose (in particular, it should not give solid products or become acid); it should retain sufficient fluidity at – 15° and should have a high flash point. The following requirements should be satisfied by such an oil: viscosity at 20°, 9·8 (Engler); specific gravity, 0·8825; flash point (Pensky), 185°; volatility, determined by heating the oil for 5 hours at 100°, should not exceed 0·06%, or determined by heating for 2 hours at 170°, should not exceed 1%.

All the oils indicated above are subdivided into numerous types indicated by numbers or letters or are sold as special brands.

Oils to be used in the open air or in cold localities should not become turbid or solidify at a temperature somewhat below the minimum to which they may be exposed. As a rule American oils solidify at 0° or a little below, whilst those from Russia do not solidify above – 10° or – 20° or even lower.

as sulphuric acid). In dark oils, the acidity may reach 0·3% or, i
cases, 0·5%, but usually it does not exceed 0·15%. Mineral acic
be present.

## RESIDUES

The bituminous and pitchy residues from the distillatio
oils (mazut, astatki or ostatki) are blackish, only slightly tr
varying consistency, and of characteristic bituminous odour d
position products of difficultly volatile hydrocarbons.

The determinations and tests usually made are those of w
gravity, distillation, flash and ignition points, viscosity, s
pitch and asphalt, the methods described for heavy oils bein
the calorific power and the sulphur are determined as in cru

As regards *distillation*, these residues often decompose at h
tures with formation of more volatile products, so that distil
methods already indicated may yield an amount of distillate
the true value. This inconvenience is obviated by distillin
of the oil at reduced pressure (about 30 mm.)[1] from a half-lit
a side-tube connected with a sloping condenser, the lower
passes through a cork in the neck of a distilling flask similar
for the distillation of crude petroleum and having its side-
munication with an ordinary water pump. The distillation
until the thermometer marks 220°, the distillate being col
second flask; at the end of the operation, air is allowed into t
and the flask containing the distillate detached, the residu
distilled up to 300–310° at the ordinary pressure.

In determining the *flash point*, the residues often froth up
ture near 100° and overflow the vessel. In such cases the
dehydrated as indicated for heavy oils. Extinction of the fl
100° may be caused by residual traces of water in the produc

When the residues are to be used as fuel, the essential dete
those of the calorific power and sulphur; the calorific value is
calories.

## VASELINE

*Vaselines* of two sorts are sold: the *natural* ones, which co
carbons semi-solid at the ordinary temperature, have colours
white to yellowish-brown, exhibit slight fluorescence and ar
somewhat sticky and ropy; and the *artificial* ones, which consi

follows :

**1. Suspended Impurities.**—These are recognised by their appearance and are separated by fusing the product and filtering it in an oven.

**2. Mineral Matter.**—From 0·5 to 1 gram is burnt in a platinum dish to ascertain if anyweighable residue remains. Any emission of odours of resin or of burnt fats during the combustion should be noted.

**3. Solubility in Alcohol. Reaction.**—One volume of the vaseline is shaken with two volumes of alcohol, the latter being separated and tested as to acidity or alkalinity and diluted with water to see if it becomes turbid.

**4. Behaviour towards Sulphuric Acid.**—10 grams of the melted vaseline are heated with 2·5 c.c. of a mixture of 5 parts of water with 15 parts of conc. sulphuric acid on a water-bath for 15 minutes, with frequent shaking, any browning of the acid or vaseline being noted.

**5. Detection of Fats.**—2 grams of the vaseline are boiled with a few c.c. of caustic soda solution, the cold aqueous layer being subsequently filtered off and acidified with hydrochloric acid : turbidity or separation of solid substance indicates the presence of fats.

**6. Detection of Resins.**—By Morawski's reaction (*see* Heavy Oils, Chemical Tests, 7).

**7. Viscosity.**—By means of Engler's viscometer (*see* Heavy Oils, Physical Tests, 7), working at 60° C. and keeping also the vessel into which the liquid flows hot.

**8. Determination of the Paraffin Wax.**—In a thin-walled, glass cylinder, 20 cm. tall and 3·5 cm. wide, a weighed quantity of about 0·5 gram of the vaseline is dissolved in the hot in 3 c.c. of ether, and the solution treated with 50 c.c. of 98% alcohol. After being cooled to 0° for an hour and filtered through a filter also kept at 0°, washing with a total quantity of 150 c.c. of 98% alcohol maintained at 0° (*see* Figure, p. 338), the insoluble residue is dissolved on the filter in hot benzene and the solution evaporated in a tared glass dish and the residue weighed. If the precipitate formed in the tube by addition of alcohol to the ethereal vaseline solution is not readily detached from the glass (as happens especially with natural vaselines and with those containing ceresine), the adherent part should be dissolved in benzene and this solution added to that previously obtained.

⁂

*Pure vaseline* should melt to a clear liquid and should not contain mineral matter, or dissolve appreciably in cold alcohol, or exhibit an acid or alkaline reaction, or turn sulphuric acid brown. According to the Italian Pharmacopœia, pure vaseline for pharmaceutical use should be perfectly neutral and quite free from fats, and should leave no ash.

*Natural* vaselines have viscosities varying from 4·5 to 7·5 at 60° C. (referred

*Crude paraffin wax* is coloured more or less intense yell whilst the *refined* product is a white or faintly yellow, tran The following tests are made :

**1. Suspended Impurities. Reaction. Behaviour to phuric Acid.**—As with vaseline (*q.v.*, 1, 3 and 4).

**2. Melting and Solidifying Points.**—The melting po mined as with fats, use being made of a capillary tube blown i to a bulb and with the lower end bent upwards after the s been introduced (*see* Fatty Substances, 4).

The solidifying point is determined with the Shukoff app 49),[1] consisting of a wide-mouthed bottle in which is fixed, a stopper, a tube of the dimensio shown. Through the stopper of t passes a thermometer reading to

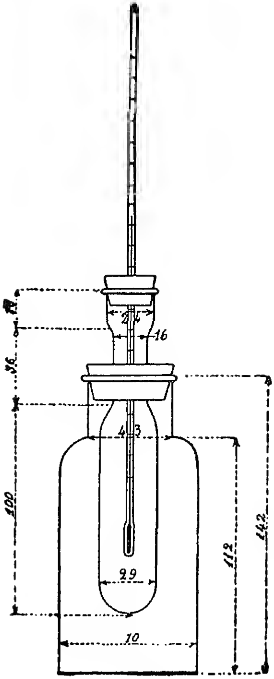


FIG. 49

In the inner tube 30–40 grams duct are melted, and when the ter the fused mass is about 5° above ing point, the apparatus is shake and regularly until the contents distinctly turbid and opaque. is then discontinued and the observed.

The solidifying point is taken perature at which the thermom stationary during the cooling o paraffin, or as the maximum ter which it rises after a short arrest When no large amount of stearic sent, only the temperature at whic cury remains stationary is observ

**3. Determination of the Pa** (in the crude product).—This is Holde's method. From 0·5 to 1 substance is dissolved in the necess of ether, an equal volume of absolute alcohol being added an cooled to −20°, the subsequent procedure being as describe petroleum (Chemical Tests, 4). The percentage found is inc to correct for the amount dissolved in the solvents.

With soft paraffin waxes this method gives less exact although results.

ith about 200 c.c. of approximately 95% alcohol ; the liquid is filtered, cohol evaporated off and the residue examined. A yellow or brown indicates the probable presence of resin, recognisable by the reactions for heavy oils (Chemical Tests, 7) ; a white residue probably consists ric acid. In any case the nature of the residue may be ascertained ermining the acid and saponification numbers.

**Detection of Carnauba Wax.**—This is often added in small pro- 1 to paraffin wax to raise its melting point. Indications of its presence ven by the characteristic aromatic odour and by the saponification r (zero for pure paraffin wax). When, therefore, the product has a fication number, it is tested for carnauba wax, the following method employed : 10 grams of the wax, chopped as finely as possible, are d for some hours with about 500 c.c. of ether, with frequent shaking. iltration, the insoluble residue—in which the carnauba wax is con- ted—is washed with ether, pressed between absorbent paper and the air to dry. The saponification number is then determined and, ence of carnauba wax, is markedly higher than that of the original ice. In doubtful cases the residue may be again treated with ether, to obtain a residue still richer in carnauba wax.

e melting point of the insoluble residue is also determined, this being erably higher than that of the original material if carnauba wax is :. Finally, the carnauba wax may be identified by decomposing the btained by means of an acid and determining the melting point of parated fatty acids.

**Detection of Coal-tar Colours.**—Any colour in the paraffin wax es that a coal-tar colour may be present. To confirm this, the pro- extracted with alcohol and the solution tested as usual (*see* Coal-Tar s).

⁂

*ned paraffin wax* should be white or only faintly yellow, neutral and free ispended impurities, and should not render sulphuric acid appreciably The melting point varies somewhat : ordinary hard paraffin waxes melt at 50–60°, whilst soft ones melt below 50° and in some cases at 30°. other hand, paraffin wax melting considerably above 60°, like that from s occasionally found, but in general a product melting below 60° may be d as a paraffin wax, and one melting between 60° and 66° as a mixture ffin wax and ceresine (*see* later). Such limits are not valid if carnauba present, 5% of this sufficing to raise the melting point by several degrees.

## CERESINE

with hot alcohol, allowing to cool, filtering, and evaporati

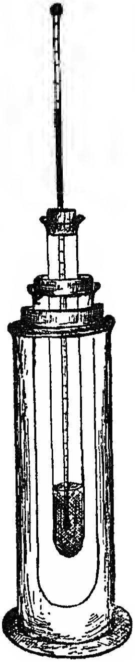


FIG. 50

of the filtrate on a slide. A crystalline app residue under the microscope indicates the considerable proportion of paraffin wax.

(*b*) DETECTION AND DETERMINATION BY VENTS (by *Armani* and *Rodano's* method) [1] : based on the different solubilities of par ceresine in a mixture of absolute alcohol a equal proportions.

Use is made of the apparatus represented consisting of a simple test-tube closed by a nelled to admit air and with a thermometer passing through it ; the tube is surrounded larger one and by a glass cylinder on a foot. containing 0·1 gram of the product is dissolve the hot solvent, is placed in position and slowly, the temperature being noted at whi tation of the dissolved substance takes place by the appearance of either a turbidity or, wi wax or ceresine, a slight crystalline layer. difference of 25° between the temperature of paraffin wax (25°) and that of ceresine (50° of even small proportions of paraffin wax tained, while the percentage may be estimated by means of the following table :

| Paraffin Wax. % | Ceresine % | Temperature of Precipitation. | Paraffin Wax. % | Ceresine. % |
|---|---|---|---|---|
| 0 | 100 | 50° | 70 | 30 |
| 10 | 90 | 48 | 75 | 25 |
| 20 | 80 | 47·5 | 80 | 20 |
| 30 | 70 | 47 | 90 | 10 |
| 40 | 60 | 44·5 | 95 | 5 |
| 50 | 50 | 43 | 100 | — |
| 60 | 40 | 41·5 | | |

4. **Detection of Resins and Fatty Acids.**—*See* Paraffi
5. **Detection of Carnauba Wax.**—*See* Paraffin Wax,
6. **Detection of Coal-tar Colours.**—*See* Paraffin Wa
7. **Detection of added Mineral Matter.**—This may

a product with m.pt. above 66° is regarded as pure ceresine. Such
.re, however, not valid if the ceresine contains carnauba wax.

## MONTAN WAX

### (Bergwachs)

*ntan wax* is obtained by the treatment of the lignites of Saxony. In
earance it resembles ozokerite or mineral wax, but in composition it
letely different.

*de montan wax* is black or dark brown, but the *purified* product is
or yellowish and of fibrous-crystalline appearance.

e determinations made are usually as follows:

**Melting Point.**—As for paraffin wax (*q.v.*, 2).

**Acidity.**—The product is dissolved at a gentle heat in a mixture
l and amyl alcohols (1 : 2) and the solution titrated with decinormal
um hydroxide solution in presence of phenolphthalein (Holde's
d).

**Saponification Number.**—About 2 grams of the wax are boiled
hours in a reflux apparatus with 40 c.c. of benzene and 25 c.c. of
rmal potassium hydroxide, the excess of the latter being subsequently
d with a seminormal acid.

**Unsaponifiable Substances.**—2 grams of the wax are saponified
ve, the solution evaporated to dryness on a water-bath with 30 grams
nular sand, and the residue extracted in a Soxhlet apparatus with
eum ether.

de montan wax has m.pt. 80–84°, acid number 18–28, saponification
r 80–90; the purified product has m.pt. 83–84°, acid number 93–100,
ponification number 94–106.

## LUBRICANTS

sides heavy mineral oils and vegetable and animal oils and fats (*see*
ponding chapters), use is made as lubricants of mixtures of mineral
th fatty oils (*see* Heavy Mineral Oils) and of complex mixtures which
ontain fats, resins, alkaline and alkaline-earthy soaps, mineral oils,
and tar oils, in addition to water and mineral matter (lime, talc,
te, etc.).

these complex lubricants the principal ones are the *stiff lubricants*,
include *cart-grease* and usually contain mineral or resin oils with
oaps and mineral substances, and the *emulsive lubricants*, formed of

alcohol, water is present. The smell emitted when the subs
on platinum foil gives an indication concerning the prese
oils, resins and fats. If ash is left, a little of the lubricant
a mixture in equal proportions of petroleum benzine and ab
the liquid being filtered after standing for some hours : the ir
is investigated for lime and other extraneous mineral subs
ordinary methods.

**2. Melting Point.**—This is determined empirically and
as follows : The cylindrical bulb of a thermometer is covere
stance, without heating, until the shining surface of the
longer discernible. The thermometer passes through the
test-tube about 18 mm. in diameter, the tube being immers
bath which is gradually heated. The temperature at which
begins to melt at the surface and that at which a drop of the f
falls from the thermometer into the tube are noted.

**3. Water.**—On a boiling water-bath, 3-5 grams of the
heated in a tared glass dish with 10–15 c.c. of absolute alc
being stirred until no further frothing occurs and the liquid
When cold, the weight is again taken, the loss representing

The latter may also be determined by Marcusson's method (
leum).

**4. Acidity.**—As a rule, stiff lubricants contain excess of
however, they exhibit acidity, the latter may be determi
(Marcusson) : 10 grams of the lubricant are heated in a re
with 50–100 c.c. of a neutral mixture of 90 parts of benzine
alcohol, any insoluble residue being filtered off in the hot an
the same mixture. The filtrate is mixed with 30 c.c. of 50
the acidity measured by titration in the hot with normal
presence of phenolphthalein.

**5. Detection and Determination of Soaps.**—From 1
of the lubricant are shaken vigorously and for a long time
separating funnel, with 25 c.c. of dilute hydrochloric acid
ether ; on standing, two perfectly clear and well-separated
be formed. Both layers should be tested with litmus pape
that they are distinctly acid ; if not, more hydrochloric acid
and the liquid again shaken. The hydrochloric solution is
and tested in the ordinary way for bases, especially lime a
which occur in the soaps employed in lubricants.

The ethereal layer separated in the preceding operation
shaking with distilled water until neutral, and is then filt

a water-bath, the greater part of it being condensed. If any drops of water remain in the flask, they are eliminated by heating on a boiling water-bath after addition of a few c.c. of alcohol. The flask is again weighed when cold, the increase representing the fatty acids and resins present either free or combined as soaps, plus the neutral fats and non-saponifiable oils; the percentage of such substance may be denoted by $a$. The acid number is then determined on the whole ethereal extract in the flask itself; multiplication of the acid number by $\frac{a}{200}$ gives the percentage ($b$) of fatty (or resin) acids found in the free state or as soaps. If from this is subtracted the amount of free acid—calculated with the same coefficient—found as under 4 (above), the remainder represents the acids of the soap; the amount of soap is then calculated in accordance with the nature of the base it contains.

**6. Detection and Determination of Neutral Animal and Vegetable Oils and Fats.**—The liquid remaining in the flask after the determination of the acidity is heated on the water-bath for about an hour with excess of alcoholic potash and the excess of the latter then titrated; this gives the saponification number of the neutral fats present. Multiplication of this number by $\frac{a}{200}$ gives the percentage ($c$) of neutral fat.

**7. Investigation of the Unsaponifiable Matter.**—The amount of this may be ascertained from the values already obtained (5 and 6), since it equals $a - (b + c)$.

When, however, it is necessary to separate and examine it, the procedure varies according as resins or resin soaps are present or absent.

In the latter case, about 50 grams of the lubricant are shaken vigorously with at least 200 c.c. of ether in a separating funnel until the oils are dissolved. A kind of emulsion holding the soaps in suspension is thus formed and filtration of this through a large pleated filter gives a clear ethereal solution containing, besides mineral oils, resin oils and tar oils, also any fats present. The ether is distilled off—the last traces being evaporated over a boiling water-bath—and the saponification number determined on a part of the residue. If there is any saponification number, fats are present; in such case, the non-saponifiable oils are separated by saponification in the cold (*see* Heavy Oils, Chemical Tests, 5), and the mineral, resin and tar oils investigated by the methods indicated for heavy mineral oils.

When, however, resins or resin soaps are present, to separate the non-saponifiable oils, the substance is extracted with acid ether (*see* 5, above), the ether evaporated, the residue washed with 90% alcohol to dissolve the resin, the insoluble residue saponified in the cold (*see* Heavy Oils,

**8. Detection and Determination of Free Lime and o Substances.**—About 10 grams of the lubricant are treated f in a reflux apparatus with 50 c.c. of benzine and 5 c.c. of alcohol residue being collected on a filter, washed with the benzine-alc weighed and examined by the ordinary methods to see if it calcium carbonate, barium sulphate, talc, graphite and other stances.

⁂

*Stiff lubricants* vary in composition according to the uses to to be put. Those for stuffing-boxes in steam-engine cylinders of a solid fat (tallow) or of a mixture of tallow with wax and ropes contain solid fats, wax, oil, talc, etc., and those for the ch lifts, etc., are similar. Lubricants for rolling mills should mel some are composed of pitch from fats or mixtures of this with c pitch, while those with a basis of wool fat consist of partially s fat, with or without resin or acid resin oil. *Briquettes of vaselin* rolling mills, are formed from mineral oil and soda soap.

Lubricants for gearing are composed of a stiff fat with gra oil, tar, resin, wax, paraffin wax and ceresine may also be ad

Lubricants for maintaining the flexibility of belting consist o with a solid fat (tallow, wool fat, wax). Adhesive lubricants f tain, besides these fats, resin, resin oil, wool fat, etc.

Lubricants for the axles of vehicles usually contain tar oil place of mineral oil and mixed lime and resin soaps in place of fatty acids.

## 2. Emulsive Lubricants

These are colourless, yellowish or reddish, and often fluo which are mixed with water to form a kind of emulsion ; t times sold ready emulsified and then have the appearance of Besides observing the colour, transparency and odour, an the flash point, viscosity and behaviour at low temperatur Oils, Physical Tests, 5, 7 and 8), the following tests are mad (*see also* Turkey Red Oil, Chapter XI).

**1. Emulsivity.**—When shaken with water in any prop should give a milky emulsion, which should not separate oil surface even after a long rest. When left overnight at the perature, the emulsion of 5 grams of oil with 100 grams of undergo no change or should at most deposit yellowish caseo

**2. Determination of the Water and of the Volatile S** emulsive oils may contain volatile solvents (alcohol, benzin recognised by the smell or, better, by distilling the material o a fixed residue remaining after calcining indicates the presence of fixed alkali.

(*a*) In presence of Ammonia. The ammonia is determined by titrating the aqueous emulsion of the oil with N/2-hydrochloric acid in presence of methyl orange. From the amount of ammonia found, the quantity of fatty acids (regarded as oleic acid) combined with it is calculated (1 gram $NH_3 = 16{\cdot}542$ grams of $C_{18}H_{34}O_2$). The total fatty acids are then determined by boiling the emulsion of the oil with a known quantity, in excess, of N/10–sodium hydroxide solution and titrating the excess of alkali with N/10–acid. The alkali used gives the total fatty acids (calculated as oleic acid) and this quantity, less the combined fatty acids, gives the free fatty acids.

(*b*) In presence of Fixed Alkali. The free acids are determined by direct titration of the acidity in the usual way, and the total fatty acids by decomposing the soaps with hydrochloric acid, extracting the fatty acids with ether, washing the ethereal layer with water until free from hydrochloric acid, and titrating the acidity of this layer. The combined fatty acids are then given by difference. The aqueous layer is tested qualitatively for alkalies (*see also* Stiff Lubricants, 5).

(*c*) In presence of both Ammonia and Fixed Alkali. The ammonia, the fatty acids combined with it, and the free fatty acids are determined as in (*a*), the total fatty acids as in (*b*) and the fatty acids combined with the fixed alkali by difference.

**4. Detection of Unsaponifiable Substances.**—*See* Stiff Lubricants, 7.

## Chapter IX

# FATTY SUBSTANCES

Fatty substances consist essentially of combinations o
of the fatty series with glycerine, and are obtained from veget
(especially seeds and fruits) and from various parts of a
liquid at the ordinary temperature are termed *oils*, and tho

The methods of analysis of fatty substances comprise
of certain physical and chemical properties, commonly know
although they are constant only within certain limits, and als
investigations. The first part of the present chapter (*Ge*
contains descriptions of the more important determinations a
out similarly on all fatty matters. The second part (*Spe*
particularly with the more important fatty substances, the
fats, terrestrial animal fats and fats from fishes and other ma
being taken in order. For each class, tables are given sho
important data relating to the characters of the fatty su
commonly sold.

Closely analogous to fatty substances are the *waxes*, w
compounds of acids with higher alcohols rather than with g
will be treated after the fats, their general methods of ana
same.

The more important industrial products derived from fa
such as stearine, oleine, glycerine, soaps, candles, etc., wil
in the next chapter.

## GENERAL METHODS

### 1. Preparation of the Sample and Preliminary De

Before analysis, a fatty substance must be freed from
purities or water it may contain. For this purpose, a portio
is left for some time in an oven at about 60°, when it clarif
melts completely if solid. It is then filtered through one
papers, care being taken that any water collected under t
fall on to the filter.

With some fats, especially industrial fats, the water, o
matters (mucilaginous substances, residues of vegetable or
mineral matter), and total fatty subs ances have to be d

*A*. DETERMINATION OF THE WATER. A flat-bottomed dish containing about 25 grams of coarse siliceous sand, previously ignited, and a glass rod, is dried at 100–105° and weighed. About 10 grams of the sample are then weighed exactly in the dish and mixed well with the sand. The dish is then heated in an oven at 100–105° and weighed at intervals of an hour until two successive weighings are not appreciably different. The loss in weight gives the water; the residue is utilised for determination *C*.

*B*. EXTRANEOUS (NON-FATTY) IMPURITIES. An exact weight (10–20 grams) of the substance is dissolved in a beaker in petroleum ether (b.pt. below 70°) by heating gently on a water-bath. The solution is filtered through a filter dried at 100–105° and tared, the insoluble matter being washed on the filter with petroleum ether until a few drops of the filtrate leave no residue on evaporation. The filter and its contents are then redried at 100–105°, and reweighed, the increase giving the *non-fatty* matter.

This may also be deduced by subtracting water + total fat from 100.

*C*. TOTAL FATTY SUBSTANCE. The residue from *A* is placed in a filter-paper cartridge or capsule and extracted with ether or petroleum ether (b.pt. below 70°) in an extraction apparatus. The ethereal solution is collected in a tared dish, evaporated on the water-bath and the residue dried at 100° and weighed.

To obtain the total fatty matter in the case of partially saponified fats (refinery residues and similar products) it is necessary to treat with ether, to shake with dilute sulphuric acid to decompose the soaps, to wash the ethereal liquid with water, to filter and evaporate it, and to dry the residue at 100° and weigh it. In this case the process indicated for turkey red oil (2) may also be followed (*see* next chapter).

If the respective quantities of free and saponified fats are required, the substance is first extracted alone with petroleum ether, the extraction being then repeated in presence of an acid.

## 2. Objective Characters

These characters are of importance in the analysis of fats, since, from the physical condition, colour and odour, at least an approximate idea of the nature of the substance may be obtained. Thus, the smell is sufficient to indicate whether a product is olive oil, tallow, palm oil, wool fat, etc.

## 3. Specific Gravity

This may be determined by means of a Westphal balance or picnometer at 15° with a liquid fat or at a higher temperature with a solid fat. In the latter case, determinations at 100° are especially convenient; the fat is placed in a wide test-tube immersed in a paraffin bath heated at 100°.

## I. Melting and Solidifying Points

The most convenient and simple method for determining tl is as follows: Into a thin-walled glass tube blown to a small middle (*see* Fig. 51) sufficient of the fused fat is sucked to f half of the bulb. When the fat has set, the branch *b* of the t fat is bent into a **U**-shape in a small flame, and the tube ther as long a time as possible (24 hours if convenient) and, if th a low temperature, in a co is then attached by means o wire or a rubber ring to a (Fig. 52) so that the fat upper part of the bulb, ar suspended in a beaker of w slowly heated. At a certair the fat begins to melt (at tl heating is discontinued) an the walls of the bulb to c lower part of the bulb. No the temperature when the f melt and again when it is in the bottom of the bulb. peratures represent the lii which the fat melts, i.e. *point*.

The fat is then allowed t and note made of the temp it begins to solidify again ar all solid, the *solidifying poi* determined.

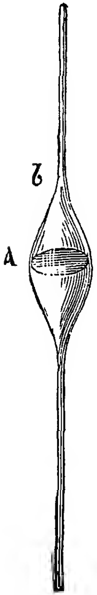


FIG. 51

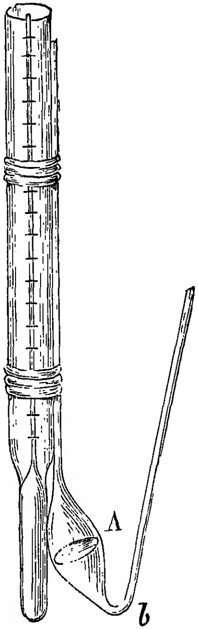


FIG. 52

The solidifying point may be determined more exactly by given for the solidifying point of fatty acids (*see* Tallow, 1, A similar method is used for measuring the melting points of the ordinary temperature and of those which become solid temperatures, but in such cases it is necessary to cool ex water and ice, with ice alone, or with a freezing mixture salt.

These methods are also used for finding the melting an points of the free acids obtained from any fat by saponifi below).

The melting and solidifying points, especially those of the

## 5. Saponification

The object of this operation is the scission of fats into their components, i.e., into acids and glycerine (or, with waxes, higher alcohols). It is effected as follows: In a conical flask or a porcelain dish, 20 grams of the fat are heated on the water-bath, with frequent stirring, with 15 c.c. of 50% aqueous caustic potash solution and 30–40 c.c. of 95% alcohol until the liquid becomes homogeneous and clear, this usually occurring after about half an hour.

With substances either containing higher alcohols (wool fat, waxes) or mixed with unsaponifiable substances (mineral oils, various extraneous matters), a clear liquid is not, however, obtained, since the action of the potash causes the separation of the higher alcohols, hydrocarbons and other unsaponifiable substances, which are usually insoluble under the conditions employed. In such a case it is well in order to ensure complete saponification to prolong the heating for an hour or more, with frequent shaking. In some instances, for example, with wool fat or waxes, it is necessary to carry out the reaction under a certain pressure. For this purpose, use is made of a round-bottomed flask, closed with a stopper carrying either a two-bulbed safety funnel charged with mercury or a right-angled tube dipping 5–6 cm. below the surface of mercury in a beaker. In other cases, for special investigations on non-saponifiable substances, *saponification in the cold* is employed; this is effected by dissolving the substance in ether or petroleum ether, adding a considerable excess of alcoholic caustic potash solution and shaking for a long time.

When the saponification is finished, the product (soap) may be used for various purposes, such as the examination of the unsaponifiable substances or higher alcohols (*see* 19: Unsaponifiable Substances), the determination of the glycerine (*see* Glycerine), or the separation of the fatty acids.

For the last purpose, the product of the saponification is first freed from alcohol by prolonged heating on a water-bath, the residue being dissolved in hot water, the hot aqueous solution shaken well with excess of dilute sulphuric acid and left at rest on the water-bath until the fatty acids are collected at the surface of the aqueous liquid in a clear layer. The water above the fatty acids is then siphoned off and replaced by fresh hot water, with which the acids are stirred, this washing being repeated three or four times. Instead of siphoning off the water, the latter and the fatty acids may be decanted on to a moist filter and the acids washed with hot water on the filter itself until the filtrate ceases to give the reaction for sulphuric acid. The washed fatty acids, in a flat dish, are kept for some time (about an hour) in a steam-oven and then filtered through a dry filter. They are then ready for various determinations, such as the melting and solidifying points, acid number, iodine number, solid and liquid acids.

The test of solubility in the ordinary solvents, e.g., in ether, if a fatty substance is pure or mixed with extraneous substanc that solvent. The test of solubility in alcohol may be used to dis oil and fatty acids in general (easily soluble even in the cold) fro of other oils and fats, which are mostly very slightly soluble, es cold.

## 7. Acid Number

### (Acidity Index)

The acid number is defined as the number of milligrams hydroxide (KOH) necessary to neutralise the free fatty acid the fatty substance. From this number the amount of free a in a fat may hence be deduced. The determination is ma

An exact weight of about 5 grams of the fat is heated in a flask on a water-bath with 50–60 c.c. of 96% alcohol,[1] and ke until the alcohol begins to boil. Seven or eight drops of pl solution (1% in 95% alcohol) are then added and the liquic decinormal potassium hydroxide solution until a persiste appears. If solid fat separates during the titration, the flas the water-bath until the fat melts. The volume of potash gives the acid number (1 c.c. N/10-KOH = 0·00561 gram I

From the acid number thus obtained the percentage o a fat may be calculated ; this is usually expressed as oleic a cular weight of which is 282 (corresponding with 56·1 of KOH lation is made by the formula,

$$x = \frac{n \times 0{\cdot}0282}{p} \times 100,$$

where $n$ is the number of c.c. of N/10-KOH used, $p$ the wei stance and $x$ the percentage of oleic acid in the substance

The free acids in a fat are sometimes expressed as sulph ($SO_3$), the formula then becoming

$$x = \frac{n \times 0{\cdot}004}{p} \times 100,$$

$x$ in this case being the percentage of $SO_3$.

EXAMPLE : For 5·223 grams of fat, 4·2 c.c. of N/10-K Since 1 c.c. of the potash corresponds with 0·00561 gram of KOH milligrams, the acid number will be

$$\frac{5{\cdot}61 \times 4{\cdot}2}{5{\cdot}223} = 4{\cdot}51.$$

---

[1] The alcohol should be

$$\text{Percentage of oleic acid} = \frac{4{\cdot}2 \times 0{\cdot}0282}{5{\cdot}223} \times 100 = 2{\cdot}267.$$

$$\text{Percentage of } SO_3 = \frac{4{\cdot}2 \times 0{\cdot}004}{5{\cdot}223} \times 100 = 0{\cdot}321.$$

The acidity of a fat may also be expressed in *degrees*, which are distinguished as *Köttstorfer* and *Burnstyn* degrees. The former represent the number of c.c. of normal KOH solution necessary to neutralise the free acidity of 100 grams of a fat.

Burnstyn degrees (formerly used, especially to express the acidity of lubricating oils) represent the number of c.c. of normal KOH required to neutralise the acidity of 100 c.c. of oil, the test being carried out as follows: 100 c.c. of the oil are shaken with 100 c.c. of 90% alcohol; when the latter has separated and become clear, 25 c.c. of it are titrated with normal KOH, tincture of turmeric or phenolphthalein being used as indicator. The number of c.c. used, multiplied by 4, gives the Burnstyn acidity of the oil.[1]

Interconversion of the acidities expressed in different ways may be effected by means of the following table:

| Acid Number (mgrms. KOH per gram of substance). | Oleic Acid. % | Sulphuric Anhydride. % | Köttstorfer Degrees (c.c. N–KOH per 100 grams of substance). |
|---|---|---|---|
| 1 | 0·5027 | 0·0713 | 1·782 |
| 1·9893 | 1 | 0·1418 | 3·546 |
| 14·0250 | 7·0500 | 1 | 25·000 |
| 0·5610 | 0·2820 | 0·0400 | 1 |

The acid number of fatty substances is very variable. As a rule, fresh or recently-prepared fats contain little or no free acid. With keeping, especially if not well protected against the simultaneous action of air and light, the acidity increases, slowly at first and more rapidly later. The acid number is of importance in judging edible oils and lubricants, neither of which should contain more than certain limiting proportions of free acid.

## 8. Saponification Number

By saponification number is meant the number of milligrams of potassium hydroxide (KOH) necessary to saponify completely 1 gram of a fatty substance. From this number the quantity of total acids, either free or combined, in a fat may be deduced. The determination is made as follows.

Reagents required are:

(1) *Alcoholic caustic potash solution* (about seminormal). Prepared

being emptied always in the same way. The flask is closed through which passes a glass tube about a metre long to se condenser and heated on a boiling water-bath, with occas for half an hour or rather more (*see* Saponification, 5).

The flask is then removed from the bath and the excess of ing free titrated with seminormal hydrochloric acid in pr drops of the phenolphthalein solution.[1]

A *check* experiment with 25 c.c. of the caustic potash (without fat) is made at the same time and under the sam the actual test.[2]

From the difference between the volumes of seminorma acid used in the check experiment and in the actual test wi amount of potash (milligrams) necessary for the complete of 1 gram of the fat is calculated.

EXAMPLE: 1·524 gram of a fat, saponified with 25 c.c. of a required 11·9 c.c. of seminormal hydrochloric acid to neutrali potash. In the check experiment, 22·5 c.c. of the acid were c.c. of alcoholic potash. Since 1 c.c. N/2-HCl = 0·02805 gra amount of KOH necessary to saponify 1·524 gram of fat is (22 gram = 0·2973 gram, so that the amount for 1 gram of fat is 0· saponification number of the fat is hence 195.

The saponification number is of importance for distingu different fats and waxes and especially for the analysis of m substances with non-saponifiable matter (mineral oils, resin oi

The majority of fatty substances have a saponification num and 200, but the oils of the Cruciferæ (colza oil, ravison oil, grapeseed oil, and a few other oils, have values below 190.

Coconut oil, palm-kernel oil, certain other vegetable fats, numbers above 200. Waxes have very low saponification numb

## 9. Ester Number

The ester number denotes the number of milligrams of necessary to saponify the neutral fat (neutral esters) in one substance. With fats which do not contain free acids, th is equal to the saponification number; when, however, free ac

---

a little powdered calcium carbonate at such a rate that 50 c.c. pass o To test the distilled alcohol, 10 c.c. are boiled with 1 c.c. of 50% caust and the liquid allowed to stand for 20 minutes to see if any colour the alcohol is unsuitable for preparing alcoholic potash and should with permanganate.

[1] When the fat gives a highly coloured solution with the alcol advisable to dilute the liquid considerably with neutral alcohol b order that the neutral point may be determined with accuracy.

the ester number is given by the difference between the acid and saponification numbers.

The ester number has importance especially for the analysis of beeswax.

## 10. Volatile Acid Number (Reichert-Meissl Number)

By this is meant the number of c.c. of decinormal alkali necessary to neutralise the volatile acids, soluble in water, obtained from 5 grams of a fatty substance under definite conditions.

Reichert's original method has been modified in various ways, the modification proposed by Leffmann and Beam and by Polenske being now preferred.

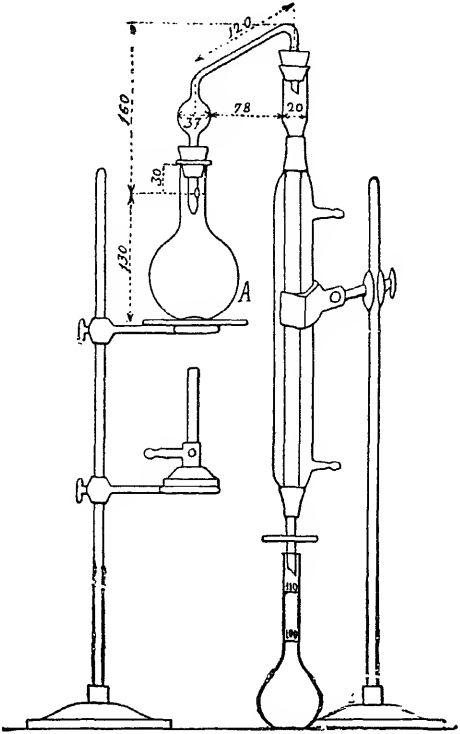


FIG. 53

In a flat-bottomed, 300 c.c. flask of resistant glass (A), exactly 5 grams of the fatty substance (filtered oil or molten fat) are heated over a small flame with 20 grams of pure glycerine and 2 c.c. of caustic soda solution (100 grams of pure sodium hydroxide in 100 grams of water) until the liquid froths and becomes clear and homogeneous (5–8 minutes). The liquid soap thus obtained is allowed to cool to 80–90° and is then shaken with 90 c.c. of distilled water at the same temperature, and heated if necessary, until solution is complete. 50 c.c. of dilute sulphuric acid (25 c.c. of the pure conc. acid to the litre) and 0·6–0·7 gram of roughly powdered pumice are then added and the liquid distilled into a 110 c.c. flask.

For this distillation the condenser and accessory apparatus have the form and dimensions (m.m.) shown in Fig. 53. The distilling flask is supported on an asbestos card on a ring 6·5 cm. in diameter, and the flame should be required, increased by one-tenth, represents the volatile aci

For each series of determinations a blank experiment r
with the same glycerine (20 grams), sodium hydroxide sol
and sulphuric acid (50 c.c.) and under the same conditions as
test. The number of c.c. of N/10-alkali used in this blan
is subtracted from the volume used in the actual test.

The determination of the volatile acid number may be car
with that of the Polenske number (*see* Butter, 15, in Chapter

The Italian official method for determining the volatile ac
for oils, Wollny's modification of the Reichert-Meissl method, a
Leffmann and Beam's modification, which differs from that de
in using a glycerine and soda solution previously prepared (125 c
and 25 c.c. of 5% sodium hydroxide solution heated until the wate
in place of glycerine and soda separately, and in a few other

The volatile acid number is of importance in the analysis of
number of fats, principally butter. With most oils and fats,
less than 1; coconut oil, palm-kernel oil, croton oil, cacao but
other fats have numbers above 1 (up to 14), while for butter tl
Some fish oils and other marine animal oils (dolphin, whale) hav
sometimes moderately high volatile acid numbers.

## 11. Acetyl Number

This represents the number of milligrams of potassium hy
sponding with the quantity of acetyl ($C_2H_3O$) combining wi
fat or wax, or, more usually, with 1 gram of fatty acids or h
(unsaponifiable substances) obtained from a fat or wax.

This number is determined as follows: About 20 grams of
or of the free fatty acids obtained in the manner described un
fication" (*see* 5, above) or of unsaponifiable substances (high
obtained as indicated under "Non-saponifiable Substances" (
are boiled for 2 hours with an equal volume of acetic anhyd
fitted with a reflux condenser, the mixture being subsequent
to a beaker, mixed with 500 c.c. of hot water and boiled for
The supernatant water is then siphoned off and the residue
in the same way, this treatment being continued until the wa
becomes acid; this usually requires four or five washings. T
product is then filtered through a dry paper in an oven at 1
for the determination of the acidity number—known as the *ac*
—and the saponification number—the *acetyl saponification*
acetyl number is given by the difference between these two

For these determinations, 3-5 grams of the acetylated

KOH, the acetyl acid value being therefore

$$\frac{485{\cdot}2}{3{\cdot}402} = 142{\cdot}6.$$

After addition of a further quantity of 30 c.c. of N/2-KOH and boiling, 11·5 c.c. of N/2-HCl were necessary to neutralise the excess of potash. The potash consumed in the saponification of the acetyl compounds was hence 30–11·5 = 18·5 c.c., corresponding with 18·5 × 0·02805 = 0·5189 gram KOH ; for 1 gram of acetylated acids the amount of KOH will be

$$\frac{518{\cdot}9}{3{\cdot}402} = 152{\cdot}5.$$

The acetyl number is therefore 152·5, and the acetyl saponification number, 142·6 + 152·5 = 295·1.

The acetyl number is related to the quantities of hydroxylated acids and higher alcohols in the fatty substances, these being especially large in castor oil, grapeseed oil, waxes and blown or oxidised oils. It is consequently of some importance for the identification of these fats and for the analysis of waxes.

## 12. Iodine Number

This expresses the number of grams of iodine 100 grams of a fatty substance are capable of fixing under definite conditions. It may be determined in the two following ways :

*A.* **Hübl's Method.**—REAGENTS required :—

1. *Iodine solution.* 25 grams of iodine are dissolved in 500 c.c. of 95% alcohol (puriss.) ; in another 500 c.c. of the same alcohol, 30 grams of mercuric chloride are dissolved and the solution filtered, if necessary. The two solutions are stored separately in tightly stoppered bottles in a cold dark place, equal volumes of them being mixed in the quantities required for the number of tests to be made, about 48 hours before use.

2. *Potassium iodide solution.* 10 grams of potassium iodide (puriss.) quite free from iodate are dissolved in 100 c.c. of water.

3. *Starch solution.* 1 gram of starch is made into a paste with a little cold water and then poured into about 300 c.c. of boiling water, stirred and left to settle ; when cold, the clear supernatant liquid is poured off for use as indicator. *Soluble starch* also may be employed, this being prepared by digesting potato starch with dilute hydrochloric acid (D 1·05) for a week, then washing with water by decantation until the washing water is free from hydrochloric acid and drying between filter-papers at a moderate temperature ; 1 gram of this starch is dissolved in 100 c.c. of hot water.

4. *Sodium thiosulphate solution.* 25 grams of crystallised sodium thiosulphate (puriss.) are dissolved in distilled water to 1 litre, and the strength of the solution determined by Volhard's method, as follows : 20 c.c. of a solution containing 3·86 grams f pu potassiu dichro-

acid, the number of c.c. of thiosulphate used corresponds
of iodine.

5. *Chloroform,* which should be pure.

PROCEDURE. In a thin glass bulb the fatty substance (as
or fused if a solid, but always previously dehydrated and f
Preparation of the Sample) is weighed, 0·1–0·2 gram being ta
oil, 0·2–0·3 gram of a semi-drying oil, 0·3–0·4 gram of a no
0·4–0·8 gram of a solid fat. The bulb is placed in a half-li
with a tight ground stopper, the bottle being held obliquel
shaken so as to break the bulb against the walls. The fat is
in 15 c.c. of chloroform and treated with 25 c.c. of the m
volumes of the iodine and mercuric chloride solutions (pre
hours earlier), care being taken in all cases to empty the pipe
way so that exactly the same volume of solution is used.
carefully shaken and the bottle stoppered and kept in a d
(15–18°) for 4–6 hours with non-drying or semi-drying oi
hours with drying oils. At the end of this time, 15–20 c.c. o
iodide solution are introduced, the stopper, neck and wall
being washed with this solution and with about 200 c.c. of
subsequently added. The excess of iodine is then titrated
sulphate solution, which is slowly run in until the aqueous
chloroform beneath appear only pale yellow; about 5 c.c
solution are then added and the titration completed.

This test is always made in duplicate and at the same
experiments are carried out with the same proportions o
under the same conditions, but without the fatty substance.
of iodine in the two checks are titrated one before and
the actual test, the mean value being taken.

This mean is deducted from the mean value obtained ir
the fat, the remainder representing the amount of iodine a
fat, and this, calculated as percentage, is the iodine numb

*B.* **Wijs's Method.**—In this method, the alcoholic sol
and mercuric chloride is replaced by an *acetic acid solution*
*chloride* prepared as follows:

8 grams of pure iodine trichloride and 8·5 grams of
solved separately in pure glacial acetic acid (99%) on a wa
dry, closed vessels to avoid absorption of moisture. Whe
solutions are transferred to the same 1-litre flask and mad
with pure glacial acetic acid.

It is necessary to ascertain that the acetic acid is at leas of contact of the fatty substance with the iodine solution is reduced bout an hour for non-drying or but slightly drying oils and fats and to t two hours for the others. The calculation is made as with Hübl's iod.

XAMPLE: For 0·352 gram of olive oil 24·90 c.c. of thiosulphate were ed, and in the check experiment, 48·80 c.c. The quantity necessary to orise the excess of iodine is, therefore, 48·8 — 24·9 = 23·90 c.c. ssuming that 0·2 gram of iodine corresponds with 16·5 c.c. of thiosulphate, ·01212 gram with 1 c.c., the amount of iodine absorbed by 0·352 gram e oil is 23·9 × 0·01212 = 0·2896 gram, so that the iodine number is

$$\frac{0{\cdot}2896 \times 100}{0{\cdot}325} = 82{\cdot}27.$$

s a rule the iodine numbers obtained by the second method (Wijs's) are r higher than those given by Hübl's method.

he determination of the iodine number is of great importance for the analysis ty substances, since it serves to characterise many of them and to indicate ey are pure or mixed. Drying oils (linseed, hempseed, walnut, poppy- madia, Japan wood, etc.) and fish oils (sardine, anchovy, herring, cod) very high iodine numbers, which usually exceed 120. The non-drying olive, arachis, almond) have iodine numbers below 100. The semi-drying colza, cottonseed, sesamé, maize) have intermediate values. Iodine num- between 30 and 60 are usually shown by vegetable fats, excepting coconut alm-kernel oil and certain so-called vegetable waxes (myrtle, Japan), have values below 11. With the animal fats the iodine number is not high, being usually less than 90.

ith each individual fat the iodine number may vary between fairly wide , in accordance with the method of preparing the fat, with the degree turity of the fruit or seed yielding it, with the conditions of storing and f the fat, etc. Very wide variations are, however, exceptional, and in cases the iodine number keeps moderately constant (*see*, for example, Oil), so that it may be used for the approximate determination of the ctive quantities of fats in a mixture of two of known character—the calcu- being made according to the law of mixtures.

e causes of pronounced variations in the iodine number are various, but ecial importance are the age and storage conditions of the fat. In general, nd badly stored (rancid) fats have iodine numbers lower than those of orresponding fresh and well-kept fats; this is notably the case with drying vhich readily absorb atmospheric oxygen.

## 13. Absolute or "Inner" Iodine Number

his represents the weight of iodine absorbable by 100 parts of the l fatty acids obtainable from a fatty substance.[1] It is determined e liquid fatty acids isolated by Tortelli and Ruggeri's process (*see* later:

and lower in the non-drying oils (about 100). For animal fa usually 90–100, but in rare cases slightly exceeds 100 (in some This number is of especial importance in the analysis of lard a (*see* Lard).

## 14. Insoluble, Fixed Fatty Acid Numl

## (Hehner Number)

This number represents the quantity of non-volatile fatt in water contained in 100 grams of a fatty substance. I is carried out as follows :

5 grams of the fat, weighed into a conical flask, are c.c. of 90% alcohol and 5 c.c. of 50% caustic potash solu is closed with a stopper through which passes a long glass reflux condenser and is then heated on a water-bath with until saponification is complete. The stopper and tube a and the alcohol distilled off, the last traces being expelle flask in a boiling water-bath. The soap is dissolved in 150 and then decomposed with a slight excess of dilute sulp flask is then left on the water-bath until the fatty acids a homogeneous layer at the surface, after which it is allow what and kept in cold water (at 10–15°) for about an hour, acids set to a solid mass. The aqueous liquid is then fi smooth, thick paper filter, previously dried at 100° and weig bottle. A further quantity of 200 c.c. of hot water is ad which is shaken, left on the water-bath for 15 minutes, somewhat and placed in cold water, the aqueous liquid before. This treatment is repeated five or six times unt longer reddens a litmus paper immersed in it for 10 min acids are then completely melted by addition of a little b the whole transferred to the filter, the flask being freed fro of the fatty acids by several small quantities of hot water that a few drops of water always remain under the acids on all the acids are on the filter, all the water on the latter i away and the filter immediately placed carefully in the which is dried at 100° and weighed at the end of each ha difference between two successive weighings is less than I weight of the fatty acids thus obtained, calculated for I stance, gives the insoluble fixed acid number sought.[1]

The insoluble fatty acid number varies little for most oi usually 95–96·5 for oils and 94·5–97 for f ts. Some vegetabl

The determination of the quantity of hydroxy-acids contained in a fatty substance is effected by Fahrion's method, based on the insolubility of the hydroxy-acids and the solubility of all the fatty acids, in light petroleum.

From 3 to 5 grams of the fatty substance are saponified in the usual way (*see* 5 : Saponification), the alcohol evaporated, the soap dissolved in 50–70 c.c. of hot water, decomposed in a separating funnel with dilute hydrochloric acid, shaken well with 100 c.c. of petroleum ether (boiling below 80°) and left until the two separate layers are perfectly clear. The aqueous layer is run off and then the petroleum ether, the insoluble hydroxy-acids, which remain adherent to the walls of the funnel, being washed several times with petroleum ether and afterwards dissolved in boiling alcohol. The alcoholic solution is evaporated to dryness in a tared dish and the residue dried at 100° and weighed.

This method allows of the determination of the hydroxy-acids produced by the oxidation, either natural or artificial, of an oil or fat. Such a determination has special importance in the analysis of boiled linseed oil and of the so-called blown oils, which are rich in hydroxy-acids.

## 16. Lactones or Internal Anhydrides

The simplest method of determining the content in internal anhydrides of a mixture of fatty acids is based on the following principle : in a mixture of pure insoluble fatty acids it is found that the acid number is equal to the saponification number, so that there is no ester number. If, however, the fatty acids are accompanied by lactonic anhydrides, the saponification number differs from the acid number. This is because the fatty acids are saturated immediately in the cold by potash, whilst the lactones must be boiled with excess of alcoholic potash in order to be neutralised.

Hence, to ascertain the content in lactones of a mixture of fatty acids, it is sufficient to determine by the ordinary methods the acid number and the saponification number and, consequently, the ester number. From the latter the content of lactone may be calculated, when the molecular weight from which the ester number is calculated is known (usually the lactone content is calculated as stearolactone).

In order that the acid, saponification and ester numbers of the fatty acids may not be confused with the respective numbers for the fatty substances, it has been proposed to call the former : *Constant acid number*, *constant saponification number* and *constant ester number*.

EXAMPLE : If a mixture of fatty acids gives the constant acid number 160 and the constant saponification number 195, the constant ester number hydroxystearic acid.

## 17. Determination of the Glycerine

The simplest method of determining if glycerine is presen is to heat a little of the latter to boiling with a few crysta bisulphate : in presence of glycerine, unpleasant, irritating oc are evolved, while a strip of filter-paper soaked in conce nitroprussside solution containing a little piperidine is dyed if placed in the mouth of the test-tube.

The glycerine in fatty substances may be determined *ind* that in the saponification of neutral fats 1 mol. of glyce corresponds with 3 mols. of potassium hydroxide (168·3 gra cation of the ester number (*see* 9, above) by 0·05466 also giv content. This method is, however, only applicable when t contain higher alcohols, unsaponifiable substances, etc.

To determine the glycerine *directly*, the fatty substanc saponified in the ordinary manner (*see* 5 : Saponification), t posed by an acid, the fatty acids separated by filtration, ar in the aqueous filtrate determined by one of the methods gi chapter for the quantitative analysis of glycerine.

## 18. Determination of the Solid and Liquid Fa

The fixed (or insoluble) fatty acids entering into the fatty substances may be divided into two principal groups : acids belonging to the acetic acid series and represented espe and palmitic acids (sometimes also by arachic and lignoc liquid, unsaturated fatty acids belonging to the acrylic seri less hydrogenated series and represented especially by oleic also by linoleic, linolenic and ricinoleic acids.

The best method for separating these two groups of ac the insolubility of the lead salts of the solid acids, and the of those of the liquid acids, in ether. Special methods serve tion of the individual solid acids and the individual liquid

**1. Separation and Determination of the Solid and L** For such separation Tortelli and Ruggeri's method is use

20 grams of the fat are saponified in the usual way cation), the soap being dissolved in water and the solut towards phenolphthalein with acetic acid. Meanwhile, 3 neutral lead acetate solution are heated in a conical flask liquid reaches the boil the soap solution is run into it in a t

to the sides and bottom of the flask, while the liquid becomes clear. The whole of the liquid is then decanted off and the soap washed with three successive quantities of 200 c.c. of hot water (70–80°). The water is drained off, the beaker cooled, the last drops of water adhering to the soap removed by means of filter-paper, and 220 c.c. of ether added. The flask is well shaken and then fitted with a reflux apparatus and the liquid gently boiled on a water-bath for 20 minutes with occasional shaking and subsequently immersed in cold water (4–5°) for two hours. The clear ether is filtered into a separating funnel,[1] care being taken to let as little as possible of the undissolved soap fall into the filter. The residue in the flask is then heated for 20 minutes with a fresh quantity of 100 c.c. of ether under a reflux condenser and the flask afterwards stoppered and placed on one side immersed in cold water.

Meanwhile the filter is washed with a little very cold ether which is caught in the separating funnel containing the other filtrate. The well-covered *filter is placed on one side*, while the ethereal liquid in the separating funnel is vigorously shaken with 150 c.c. of 20% hydrochloric acid to decompose the lead soap of the liquid acids and then left to stand until the ether has collected at the surface in a clear layer. The lower aqueous layer, together with the precipitated lead chloride, is run off, the treatment repeated with 100 c.c. of hydrochloric acid, and the ethereal solution then washed three times with distilled water (150 c.c. each time). Finally, the bulk of the ether is distilled off and the last traces driven off on a water-bath while a current of carbon dioxide is passed.

The liquid acids thus obtained are weighed and calculated to 100 parts of the substance. These liquid acids, provided they are kept out of contact with the air, may be further utilised for the detection of cottonseed oil and sesamé oil (*q.v.*) and for the determination of the absolute iodine number (*see* 13, above).

The lead soap of the solid fatty acids, left undissolved in the flask immersed in cold water, is collected on the filter placed on one side, as mentioned above, and washed well with very cold ether and then introduced into a separating funnel where it is shaken with ether and hydrochloric acid as in the case of the liquid acids.

The ethereal solution of the solid fatty acids is distilled and the residue dried in an oven at 100° and weighed. For greater accuracy, the weight found may be increased by the quantity of solid acids (stearic and palmitic) corresponding with their lead soap remaining dissolved in the ether, knowing that 50 c.c. of anhydrous ether at the ordinary temperature dissolve 0·0074 gram of lead stearate and 0·0092 gram of lead palmitate; these amounts correspond with 0·0054 gram of stearic and 0·0065 gram of palmitic acid.

of the liquid acids soluble, in alcohol, and (2) that of *Fach*
based on the insolubility of the solid fatty acids and their
cold acetone; this solvent also serves to separate stearic
acids from myristic and lauric acids.

The content of liquid and solid acids in a fatty substan
deduced from the absolute and relative iodine numbers. If $I$
iodine number or that of the fat as such, and $I_a$ the absolute
or that of the liquid fatty acids extracted from the fat, 1 pa
iodine corresponds with $\frac{100}{I_a}$ parts by weight of liquid acids
sponds with 100 parts by weight of liquid acids). With t
iodine $I_r$ absorbed by 100 parts of the fat there correspond
liquid fatty acids, this last fraction giving the percentage
acids in the fatty substance.

When a mixture of palmitic, stearic and oleic acids along
the content of oleic acid may be calculated from the relative
of the mixture, since it is known that the theoretical iodine n
acid is 90·07. Thus, if $I$ is the relative iodine number of th
$O$ the percentage of oleic acid sought,

$$O = \frac{100 \times I}{90{\cdot}07} \text{ or } O = 1{\cdot}1102I.$$

Lastly, it must be pointed out that, with mixtures of t
named above, the content of liquid and solid acids may be
means of the solidification point of the mixture, use being ma
table (*see* Tallow and Stearine, 1).

**2. Determination of the Stearic Acid.**—The content
in a mixture of fatty acids obtained by saponification of a fat
mined by Hehner and Mitchell's method, which is based on
stearic acid is very slightly soluble in alcohol at 0°, whilst p
much more soluble and the liquid acids readily soluble.

From 0·5 to 1 gram of the fatty acids, if solid, or 5 gram
dissolved in 100 c.c. of alcohol of D = 0·8183 (94·4% al
saturated at 0° with pure stearic acid; the solution is the
and filtered and the residue washed with alcohol saturate
acid, working always at 0°; finally the stearic acid remain
weighed.

This method is applicable especially to mixtures of stearic ac
and oleic acids, which are the most common; with more co
it does not give satisfactory results.[2]

more general case, of stearic and palmitic acids, the respective proportions of these two acids may be determined from either the acid number or the melting point of the mixture.

The following table of Mangold and Marazza gives the proportions of stearic and palmitic acids in a mixture of the two acids, on the basis of the acid number.

### TABLE XLII

### Stearic and Palmitic Acids from the Acid Number

| Acid Number (mgrms. of KOH per gram of mixture). | 100 parts of mixture contain | | Acid Number (mgrms. of KOH per gram of mixture). | 100 parts of mixture contain | |
|---|---|---|---|---|---|
| | Stearic Acid. | Palmitic Acid. | | Stearic Acid. | Palmitic Acid. |
| 197·50 | 100 | — | 208·86 | 45 | 55 |
| 198·50 | 95 | 5 | 209·95 | 40 | 60 |
| 199·50 | 90 | 10 | 211·06 | 35 | 65 |
| 200·50 | 85 | 15 | 212·18 | 30 | 70 |
| 201·50 | 80 | 20 | 213·30 | 25 | 75 |
| 202·50 | 75 | 25 | 214·45 | 20 | 80 |
| 203·50 | 70 | 30 | 215·60 | 15 | 85 |
| 204·60 | 65 | 35 | 216·77 | 10 | 90 |
| 205·60 | 60 | 40 | 217·95 | 5 | 95 |
| 206·70 | 55 | 45 | 219·13 | 0 | 100 |
| 207·77 | 50 | 50 | | | |

The following table gives the stearic and palmitic acids contained in a mixture of these two acids in relation to the melting point of the mixture, according to Heintz and according to Hehner.

### TABLE XLIII

### Palmitic and Stearic Acids from the Melting Point

| Melting Point. | | Solidifying Point. | Palmitic Acid. % | Stearic Acid. % |
|---|---|---|---|---|
| Heintz. | Hehner. | | | |
| 62·0° | 61·8° | — | 100 | 0 |
| 60·1 | 59·0 | 54·5° | 90 | 10 |
| 57·5 | 56·5 | 53·8 | 80 | 20 |
| 55·1 | 54· | 54·0 | 70 | 30 |

## 19. Unsaponifiable Substances

By unsaponifiable substances in fatty matters is usually substances which are not attacked by the alkali during the s such as mineral oils, resin oils, solid paraffin and ceresine—v saponifiable in the strict meaning of the term—and also subs are liberated by the saponification itself and separate owing solubility under the conditions of saponification, such being, the higher alcohols (ceryl and myricyl alcohols, cholesterol and

The latter substances form an integral part, i.e., enter stitution, of many fatty matters and waxes, while the former and the like) may be added artificially to fats.

To separate the unsaponifiable substances from fats it suffic in the usual way (*see* 5), to dissolve the soap in water and shak with ether or petroleum ether (b.pt. below 80°), to separate t and evaporate the ethereal solution, which will leave the matters. To prevent emulsification, which often occurs w soap is shaken with ether, a little alcohol may be added and a la of ether used.

To determine quantitatively the unsaponifiable substanc convenient and accurate to work as follows:

20 grams of the substance to be examined are boiling with 15 c.c. of 50% caustic soda solution and 50 c.c. o for about 30 minutes, the liquid being then transferred to a alcohol evaporated, 8-10 grams of sodium bicarbonate (to excess of caustic alkali into carbonate) and 70–80 grams of being gradually mixed in. When the whole is quite dry it thick filter-paper thimble and extracted in an extraction ap petroleum ether (b.pt. below 80°). The solvent is subsequen the residue, dried at 100° and weighed, giving the quantity of matter.

The unsaponifiable matters which may be extracted fro way or by the other methods given under particular cases ( Detection of Phytosterol) are mainly as follows:

**1. Higher Alcohols.**—These are divided into those of series (cetyl, ceryl, myricyl) and those of the aromatic series phytosterol). The former, which occur especially in waxes, melt at moderately high temperatures—cetyl alcohol at 50°, and myricyl at 85°; they are soluble in alcohol, from which th readily, and they dissolve in and combine with boiling acet the solution remaining liquid on cooling provided that a su solid acetyl compound which, when purified and recrystallised from alcohol, melts at 114–115°. If a solution of a little cholesterol in 2 c.c. of chloroform is shaken with an equal volume of concentrated sulphuric acid, the chloroform solution assumes a red coloration, which soon changes to cherry-red and then to violet-red, this persisting for some days, whilst the acid liquid turns reddish brown; if a few drops of the chloroform solution are shaken in a porcelain dish, the colour changes successively to blue, green and dirty yellow.

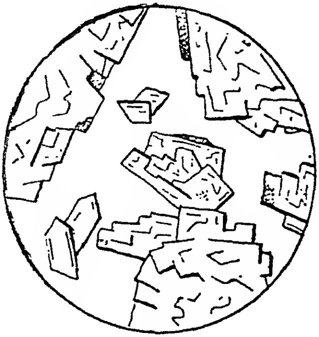


FIG. 54

*Phytosterol* or *sitosterol* (*cholesterol from plants*) occurs in fatty substances of vegetable origin. It dissolves in alcohol, from which it crystallises in tufts of broad, blunt-ended needles, having the microscopic appearance of elongated, blunted plates (Fig. 55), m.pt. 135–144°. When boiled with acetic anhydride, phytosterol also gives an acetyl-compound, m.pt. 125–137° (purified and recrystallised). With chloroform and sulphuric acid it behaves like cholesterol.

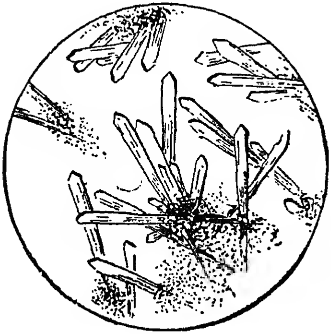


FIG. 55

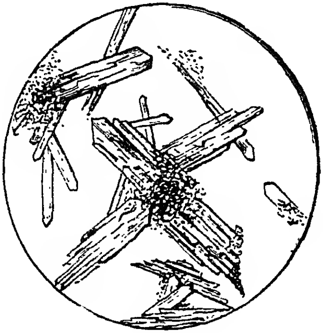


FIG. 56

When a mixture of cholesterol and phytosterol—which may be obtained from a mixture of animal and vegetable fats or oils—is crystallised from alcohol, the crystals show the predominant form of the phytosterol (Fig. 56) and melt at temperatures intermediate to the melting points of cholesterol and phytosterol (*see also* Lard).

**2. Paraffin Wax. Ceresine.**—These are solid and are insoluble in alcohol, aniline and acetic anhydride,[1] and hence distinguishable from the resin oils dissolve.

## 20. Detection and Determination of the Re

Resin (colophony) [1] is often found mixed with fatty subst ally boiled linseed oil for varnishes and the like), waxes, anc soaps.

**1. Qualitative Investigation.**—With neutral fats or oils or waxes, 5–10 grams of the substance are heated to boiling for a with as much 70% alcohol and the alcoholic liquid allowed to off and evaporated: the colophony, which is easily solubl remains as residue and is identifiable by its general characters a of the following reaction (Morawski's):

A small quantity of colophony, dissolved in 1–2 c.c. of ace and then treated with 1–2 drops of sulphuric acid of D 1·53 sulphuric acid of 66° Baumé plus 35·7 c.c. of water), gives a tra red coloration.

A similar reaction is, however, given by cholesterol when, wool fat may be present. In such case the residue from the of the alcoholic liquid is taken up in dilute potassium hydro (which readily dissolves colophony), the liquid being shake (which dissolves cholesterol) and the aqueous alkaline liquid the resin acids thus obtained tested by means of Morawski's

With soap, about 5 grams are dissolved in water and the so with ether, the aqueous liquid being acidified and the fatty ac Morawski's reaction.

**2. Quantitative Investigation.**—When mixed with fatt or with soaps, colophony may be determined by *Twitchell's n* is based on the fact that, in alcoholic solution, the acids of not esterified by gaseous hydrogen chloride, whilst fatty acid converted into ethyl esters under these conditions. The pr follows:

The mixture of fats and resin is saponified in the usual fatty acids then separated by acidifying the soap solution. of a soap, this is dissolved in water and the solution filtered and posed by acid. With mixtures containing unsaponifiable su necessary, after saponification, to extract the liquid with benz leum ether to remove the unsaponifiable matter, the aqueous s then decomposed with an acid. The fatty and resin acids t are well washed and dried and 2–3 grams dissolved in 50 c.c alcohol and dry hydrogen chloride gas passed into the solu about 10° by immersion in water and ice. The current of g

(a) *Volumetrically.* The product of the esterification is dissolved in ether and washed repeatedly with water to eliminate the mineral acid and then diluted with 50 c.c. of neutral alcohol and titrated with N/10-potassium hydroxide in presence of phenolphthalein: 1 c.c. N/10-KOH = 0·0346 gram of resin.

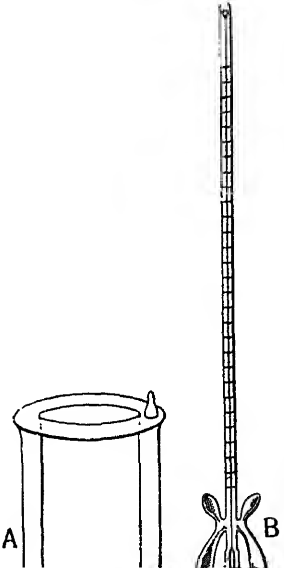
(b) *Gravimetrically.* The esterification product is dissolved in 50 c.c. of petroleum ether (b.pt. below 80°), shaken well, and the aqueous acid liquid separated. The petroleum ether solution is washed with water and shaken with 50 c.c. of an aqueous solution containing 0·5 gram of caustic potash and 5 c.c. of alcohol. The resin acids pass into the aqueous alkaline solution, whilst the fatty esters remain dissolved in the petroleum ether. The alkaline aqueous liquid is, therefore, separated and acidified, the resin acids thus obtained being removed by shaking the liquid with ether; the solvent is then evaporated and the residue dried at 100° and weighed.

This method gives only approximately exact results, which are more accurate with the volumetric than with the gravimetric method. Modifications have been suggested by Fahrion [1] and by Wolff and Scholtze,[2] but it is most commonly used in its original form. For more exact determinations, the method of Twitchell and Gladding may be used under the conditions laid down by Holde and Marcusson.[3] Another method for the determination of resin, based on the solubility of the alkali resinates in acetone, has been proposed by Leiste and Stiepel.[4]

## 21. Maumené Number

This represents the rise in temperature produced when the fatty substance is mixed with concentrated sulphuric acid under definite conditions. Various methods of measuring this increase, based on the original one of Maumené, have been suggested. Nowadays suitable forms of apparatus are used (*thermo-oleometers*), such as that of Jean[5] or that of Tortelli.

*Tortelli's thermo-oleometer* consists of a small glass vacuum-jacketed vessel *A* (Fig. 57), and a thermometer-stirrer *B* provided with two glass vanes near the bulb. 20 c.c. of the oil are pipetted into *A*, stirred for a minute by rotation of the stirrer and the temperature read (*t*). By means of another pipette 5 c.c. of sulphuric acid (D exactly 1·8413) are allowed to flow on to the oil while the stirrer is



The Maumené number is $t_1 - t$.

To obtain constant and comparable results it is necess always exactly as described and to use acid of the exact den be controlled by using 20 c.c. of distilled water in place of th 50 being then obtained by the test. The oil and acid use for some time (about 30 minutes) to attain the temperature o ing air.

In the case of a drying oil, it is convenient to dilute t with olive oil of a known Maumené value, the result obtair properly corrected.

Solid fats are used in the fused state, the acid being a temperature; allowance is then made in the calculation for specific heats.

The results obtained for drying and non-drying oils with Tor are about 8–10 higher than those given by Jean's apparatus.

The results vary with the method used for their determir the nature of the substances themselves. In general, howev fish oils and fish-liver oils give values above 100, semi- and and blubber oils, values less than 100 (usually 30–90), and anima (30–35).

Old or rancid oils and those which have been exposed to tl give values different from the fresh oils.

## 22. Drying Properties of Oils

Certain fixed oils, when exposed to the action of the a gradually dry, forming transparent and elastic pellicles like oils are described as *drying oils*. Oils which either remain fluid little, even after long exposure to the air, are *non-drying* a thicken and dry, although incompletely and slowly, are term

The drying properties of an oil depend on its power t greater or less rapidity, atmospheric oxygen, so that the dr of an oil may be determined from the quantity of oxyger from the rapidity of the absorption.

There are several methods of determining the absorp common being those of Livache and Bishop.

1. LIVACHE'S METHOD. Precipitated lead is prepared b sheet of zinc in 10% lead acetate solution acidified with washing the lead precipitate formed with water, alcohol and ing it in a vacuum over sulphuric acid. A clock-glass witl of the lead on it is weighed and about 0·5 gram of the oil

tilling the solvent, drying the residue on a water-bath and powdering it. Of this resinate, 0·2 gram is heated in a water-bath with 10 grams of the oil to be tested until completely dissolved. 1 gram of precipitated silica and a glass stirring-rod are placed in a dish and the whole tared, 1·02 gram of the oil plus resinate being allowed to fall drop by drop on to the sand and the whole weighed. The mass is well mixed and left exposed to the air at the temperature 17–25° for drying oils or 20–30° for other oils. After 6 hours and after further successive intervals of 12 hours the basin is weighed (the mass being stirred each time) until of constant weight. The maximal increase of weight, multiplied by 100, Bishop terms the *degree of oxidation* of the oil.

Drying oils usually absorb oxygen easily and rapidly, so that after an exposure of 2–3 days the absorption is practically at the maximum attainable even after 8–10 days. On the other hand, non-drying oils do not increase in weight during the first days of exposure and begin to absorb a small quantity of oxygen only after 5–6 days.

According to Livache, the maximum amount of oxygen absorbed per 100 parts of linseed oil is about 14, the amounts for walnut oil, poppyseed oil, cottonseed oil and beechnut oil being 8–5. Olive, arachis, sesamé and colza oils absorb only 1–3% of oxygen.

According to Bishop's method, the mean degree of oxidation is 17 for linseed oil, 13–15 for hempseed, poppyseed and walnut oils, and 6–9 for cottonseed, sesamé and arachis oils.

## 23. Colour Reactions.

Different fatty substances, more particularly the fatty oils, give special colorations with various reagents, such as acids, alkalies and different salts. Some of these reactions serve to distinguish certain groups of oils, whilst others, being specific for a single oil, serve to characterise the latter. These specific reactions will be dealt with in the special part in the paragraphs treating of the particular oils (*see* Cottonseed Oil, Sesamé Oil). Some of the group reactions in more general use for the distinction of the different groups of vegetable oils (for animal oils, *see* Fish Oils) will be described here.

1. HEYDENREICH'S REACTION. Five or six drops of the oil are allowed to drop from a pipette on to about 5 c.c. of pure sulphuric acid (66° Baumé) in a flat-bottomed porcelain dish. In about three minutes the oil spreads to form a very thin layer on the acid; the colour formed during this time in the zone of contact between oil and acid is observed.

With olive, arachis and almond oils, there is no sensible change of colour, the oil remaining pale yellow or yellow, although sometimes with olive oil a greenish-yellow coloration appears. With very old or rancid oils, colours tion after the mixture has been kept for 20 minutes in a bo

Olive, almond, hazel-nut and arachis oils retain thei or become somewhat paler. Olive oil may, however, so a greenish tint, especially in the cold. If these oils are r turn orange-coloured.

Sesamé, cottonseed, beechnut, linseed, walnut, colza, a etc., change to orange or brownish red.

3. Brullé's Reaction. In a test-tube 10 c.c. of the dry, finely powdered egg-albumin and 2 c.c. of pure nitr as for Hauchecorne's reaction are carefully and uniformly acid begins to boil, the whole being then shaken somewhat continued until the albumin is completely dissolved, thi few seconds.

During the boiling with the acid and albumin, olive oil entirely decolorised and after cooling forms a more or less a straw-yellow colour which persists for a long time, but sets to a solid mass of the same colour. Similar behavi arachis, almond and walnut oils.

Seed-oils, however, become deep yellow (colza, sesam to brown (cottonseed, poppyseed, maize, beechnut, linsee

4. Bellier's Reaction. 5 c.c. of the oil or filtered of pure, colourless nitric acid of D = 1·4 and 5 c.c. of a solution of resorcinol in benzene are introduced into a gr with a ground stopper and shaken for about 10 seconds, observed during the shaking and immediately afterwards

In place of the benzene solution of resorcinol, a 0·1% of phloroglucinol (*Kreis*) may be used.

Seed oils in general, and especially sesamé, cottons linseed, maize (corn oil), soja-bean and colza oils, give col from pink to red to violet to brown (with phloroglucinol red).

This reaction serves more particularly to detect vegetable s fats (lard), in lard oil, in foot oils, and also in olive oil, since and oils and olive oil give no appreciable coloration, at any seconds. After this time all oils and fats give colorations.

Practice with oils and fats of known origin is necessary i guish pure oils and fats from mixtures by this reaction.

With oils which have been subjected to long exposure to li in the air, the reaction fails.

## 24. Elaidin Test

Drying oils give an orange-yellow or brown liquid product.

## SPECIAL PART

## Vegetable Oils

vegetable oils is meant those fatty substances extracted from the ble kingdom and liquid at the ordinary temperature. These oils rly numerous but only relatively few are in common use, these includ- ve, almond, arachis, colza, cottonseed, linseed, sesamé and castor hich are treated in detail below. Table XLIV on p. 410 gives the al characters of these oils and of the other more important vegetable

## ARACHIS OIL

m the seeds of *Arachis hypogæa*. It is pale yellow and has a slight and an agreeable taste. About 15 grams dissolve in 1000 c.c. of te alcohol at 15°.

th Heydenreich's, Brullé's and Hauchecorne's reagents it gives no iable colorations, only a pale pink colour being obtained with the the cold. The other chief physical and chemical characters are given n Table XLIV.

aracteristic of arachis oil is its content of arachidic and lignoceric The detection and, if required, the determination of these acids to identify the oil and to detect its presence (approximately also antity) in mixtures with other oils.

**Detection and Determination of Arachidic and Lignoceric** .—The most convenient method for this purpose is that of Tortelli uggeri (*see* below), which, like various other methods, is based on me principle as Renard's older method.[1]

preliminary and more rapid examination may be made by the other ethods described below.

ORTELLI AND RUGGERI. 20 grams of the oil are saponified, ty acids separated, and the solid acids extracted from these by means lead salts,[2] the operations being carried out exactly as described in l method 18 (Tortelli and Ruggeri's method). The solid fatty acids btained are placed in a suitable flask, 100 c.c. of 90% alcohol and a of dilute hydrochloric acid (about normal) being added. The flask ed with a stopper through which a thermometer passes into the liquid

from pure arachis oil, the temperature at which crystals
the alcoholic solution cools is 35–38°. The melting poi
of acids obtained in this first crystallisation is usually

No other oil gives a crystalline precipitate in such
when the alcoholic solution of its solid acids (prepared a
to the ordinary temperature. Only cottonseed oil and s
Tunisian olives give a precipitate, but this is amorphous
in perfectly opaque mammillary masses, m.p. below 7
precipitate does not form in a second crystallisation.

If it is required to estimate exactly the *quantity* of
noceric acids, the crystals formed in the alcoholic solu
and washed with three successive quantities of 10 c.c. of
then thoroughly with 70% alcohol. The crystals are t
100 c.c. of 90% alcohol (or a less volume if the amount
crystallisation repeated as described above. The cryst
are collected on a filter, washed twice with 10 c.c. of 90%
with 70% alcohol until this dissolves no more; they are
a little boiling absolute alcohol, the solution being evap
dish and the residue dried at 100° for about an hour a
the weight found is added that of the arachidic and lignoce
in solution in the 90% alcohol used for the various c
washings, the following solubility coefficients (Tortelli a
employed:

| Weight of Acid obtained in grams. | Number of grams dissolved by 100 c.c. of 9 temperature of | |
|---|---|---|
| | 15° | 17·5° |
| 1·00 or more . . | 0·071 | 0·081 |
| 0·70 . . . . . . | 0·068 | 0·078 |
| 0·50 . . . . . . | 0·064 | 0·075 |
| 0·25 . . . . . . | 0·052 | 0·060 |
| 0·05 or less . . | 0·031 | 0·040 |

Arachis oil contains, on the average, 4·80% of arachidic
together, so that the proportion of these acids found by
indicates if the oil is pure or not. Further, the presence an
acids serve for the characterisation and determination of ara
with olive and other oils. In such mixtures, the crystallisat
and lignoceric acids from the alcoholic solution of the soli
place at lower and lower temperatures as the proportion

he temperature at which the first crystals form :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| rature of al precipi- n . . | 35–38° | 31–33° | 28–30° | 25–26° | 22–24° | 20–22° | 18–20° | 16–17° |
| tion of ara- oil . . | 100% | 60% | 50% | 40% | 30% | 20% | 10% | 5% |

e proportion of arachis oil in a mixture may, however, be determined exactly from the quantitative determination of the arachidic and lig- c acids, the content in the pure oil being 4·80%. In this way as little of arachis oil in admixture with other oils may be detected.

BELLIER'S METHOD (modified).[1] Into a conical flask of about 100 pacity are pipetted 1 c.c. of the oil and 5 c.c. of about 8% alcoholic c potash solution (80 grams of pure potassium hydroxide dissolved c.c. of water and made up to 1 litre with 90% alcohol). The flask is with a stopper carrying a tube 80 cm. long (to avoid loss of alcohol) eated on a boiling water-bath with continual shaking until saponifi- is complete (4–5 minutes). The liquid is then cooled to about 25° aken with 1·5 c.c. (exactly) of dilute acetic acid (1 vol. of glacial acid + 2 vols. of water), 3 drops (not more) of glacial acetic acid c.c. of 70% alcohol. If the liquid becomes turbid (as usually happens chis oil is present in marked quantity), it is gently heated until clear, sk being then closed with a stopper through which passes a ther- ter with its bulb in the liquid. The flask is then cooled and shaken vater-bath so that the temperature of the liquid becomes exactly 16°, ich it is maintained for 5 minutes with gentle shaking.

the liquid remains clear it is kept at 15·5° for 5 minutes, and if it still s clear, arachis oil is either absent or present in less proportion than The appearance of turbidity at 15·5° indicates the presence of arachis bout 5%) in the oil. With higher proportions, marked turbidity s even at 16°. With pure arachis oil, the liquid begins to show lity at about 40°.

e temperature at which the alcoholic solution of the fatty acids, obtained scribed above, first becomes turbid serves to indicate approximately the rtion of arachis oil in its mixtures with olive oil :

| | Temperature at which turbidity appears. |
|---|---|
| Pure olive oil . . . . . . . . | 11·5–14·5° |
| ,, ,, + 5% arachis oil . . . . . | 16–17 |
| ,, ,, 10 ,, . . . . . | 19–20 |
| ,, ,, 20 ,, . . . . . | 25–26 |
| ,, ,, 30 ,, . . . . . | 29–30 |
| ,, ,, 40 ,, . . . . . | 31–32 |
| ,, ,, 50 ,, . . . . . | 33–34 |
| ,, ,, 6 ,, . . . . . | 35–36 |

then decomposed with a dilute acid to liberate the fat
dissolved in petroleum ether. The solution is filtered a
the arachidic and lignoceric acids investigated by preci
alcohol in the manner of the Tortelli and Ruggeri me

**2. Detection of Adulterations.**—Commercial ar
adulterated with, or may contain as impurities, sesamé
poppyseed and other seed oils. Sesamé and cottonsee
by the reactions of Villavecchia and Fabris and of H
Oil and Cottonseed Oil), colza oil by Tortelli and For
by a lowering of the saponification number (*see* Colza
and other seed oils in general by the colour reaction
Hauchecorne, and Brullé, and by a diminution in the c
and lignoceric acids.

⁂

*Comestible arachis oil*, when fresh, should contain only
Old oils and those for industrial use are more or less acid
to about 30% of free acid (calculated as oleic acid), the us
about 20%. *Arachis oil for soapmaking* should contain
of moisture and foreign matters together and should hav
iodine number 87–100, solidification point of the fatty acids
number (Tortelli) 50·6.

The following products are also sold: *Arachis marg*
pressing the oil in the cold (m.pt. 22–25°, iodine number 7
produced by purifying the rancid oil with soda and compo
neutral oil and various impurities; and *arachis oil No.* 2, o
fication of rancid oils with ammonia. The commercial val
of the oil No. 2 depends on the content of total fatty matt
1, *A* and *C*).

## COLZA OIL AND OTHER CRUCIFERO

The more common oils of the Cruciferæ are colza
less common are those of jambo, turnip, mustard (white
seed and hedge mustard. All have very similar charac

Colza oil and ravison oil (from the seeds of *Brassica*
*napus*), which are most used, are yellow, sometimes tend
have a special, more or less pronounced odour and a
About 8 grams dissolved in 1000 c.c. of absolute alc
characters are given later in Table XLIV.

With Heydenreich's reagent they give orange colo
apparent brown striæ, especially if the containing dis
With Hauchecorne's and Brullé's reagents they give more
colorations.

'oned above, are their low saponification number (*see* Table XLIV) heir content of erucic acid. By the determination of the saponification oer and essentially by certain tests on the fatty acids these oils may entified and their presence in mixtures with other oils detected. These are as follows.[1]

. **The Tortelli and Fortini Tests on the Fatty Acids.**—These include the determinations of the melting point and iodine number of olid fatty acids and the critical solubility temperature of the sodium of the liquid acids, these characters being especially influenced by oresence of erucic acid. The solid and liquid fatty acids should first epared (*see* a) and the determinations indicated then made (*see* b and c).

a) *Preparation of the solid and liquid fatty acids.* 20 grams of the re saponified with alcoholic potash and the potassium soap converted he lead soap by the Tortelli and Ruggeri method (*see* General Methods, ). The lead soap, dried with filter-paper, is taken up with 80 c.c. of , shaken well, heated for 20–30 minutes in a reflux apparatus with sional shaking and then cooled in water at 15° for an hour. The ethereal d is subsequently decanted through a filter into a separating funnel, ttle as possible of the solid residue being introduced on to the filter. residue is heated with 40 c.c. of ether in a reflux apparatus for 20 minutes, ed at 15° for an hour, and the whole then collected on the filter, the te passing into the separating funnel. The flask and residue are washed 40 c.c. of ether. This washed lead soap, insoluble in ether, is introd into another separating funnel by perforating the filter and washing 1 with ether, of which 100 c.c. are used.

'o each separating funnel 150 c.c. of 20% hydrochloric acid are added, 'unnel being thoroughly shaken and then left at rest until the ethereal has separated well, the aqueous liquid and the lead chloride formed g run off. This treatment is repeated with a second quantity of 100 f hydrochloric acid and if necessary with a third quantity. The two real solutions are then washed twice with 100–150 c.c. of water, care taken not to shake too vigorously. The ethereal solutions are finally ed through two pleated filter-papers into two glass dishes, from which solvent is evaporated at as low a temperature as possible. In one dish solid acids (from the lead salts insoluble in ether) and in the other the d acids of the oil remain.

b) *Tests on the solid acids.* The *melting point* is determined with a tube (*see* General Part, 4) and is taken as that temperature at which substance falls into the lower part of the bulb. The *iodine number* is rmined by Hübl's method.

being heated gently, treated with slight excess of satu bonate solution, evaporated almost to dryness and driec sulphuric acid. The dry residue is powdered and purifi of admixed sodium carbonate by successive treatments c.c. of absolute alcohol, with which it is heated to boilir The liquids are filtered hot and the sodium soap separ a white or straw-yellow, caseous mass, which is pumpec vacuum over sulphuric acid. Of the perfectly dry, pow 0·5 gram is treated in a large test-tube with 20 c.c. of al tube being hung in a beaker full of water and a therm so that its bulb is in the centre of the liquid.

The liquid is then heated and continually stirred wit until a clear solution is obtained, the whole being then al taneously. At a certain point the alcoholic solution seen to contain minute crystals, which are only barely but rapidly multiply and fill the whole mass of the liquid at which the first crystals are observed is the characte perature.

When the crystallisation is well under way, the th remains stationary for some time, or at least falls wit slowness.

The sodium soap of the liquid fatty acids of colza oil l bility temperature in alcohol, 50–45° ; for other seed oils a temperature is lower (*see* later). Further, the sodium so of various seed oils are deposited with a caseous, flocculent a ance, whereas that of olive oil, at least at first, is distinct

From the melting point and iodine number of the solid critical solubility temperature of the sodium soap of the li ravison) oil may be detected and approximately estimated other oils ; the following data are given by Tortelli and

| Oils. | Melting Point of Solid Acids. | Iodine Num of Solid Acid |
|---|---|---|
| Colza oil | 41–42° | 62 |
| Olive oil | 58–59 | 7·8 |
| Colza oil, 50<br>Olive oil, 50 | 47–48 | 32 |
| Colza oil, 30<br>Olive oil, 70 | 48–49 | 28 |
| Colza oil, 20 | 50–51 | 22 |

mixed with olive oil (*q.v.*) and, in their turn, may be adulterated with other seed oils (linseed, poppyseed, cameline, hempseed, etc.), and particularly with fish oils and oils of other marine animals, as well as with mineral oils

The determination of the various characters (especially saponification, iodine and Maumené numbers) and the test for erucic acid by Tortelli and Fortini's method readily show if the oil is pure or otherwise. Seed oils in general and animal oils raise the saponification number, while linseed, hempseed and poppyseed oils raise also the iodine and Maumené numbers. Fish oils and other marine animal oils are detected by means of the test for the octabromo-compounds and the Tortelli and Jaffe reaction (*see* Fish Oils), and mineral oils by testing for unsaponifiable substances.

⁂

*Colza oil for comestible and illuminating purposes* should be well refined and not acid. *Industrial ravison oil* should have: D = 0·911–0·937, iodine number = 103–108, saponification number = 175–178, refractive index (Zeiss) at 25° = 68–71, Maumené number (Tortelli) = 60·8°.

## COTTONSEED OIL

Obtained from the seeds of *Gossypium herbaceum*. It is yellow or golden-yellow or, if not well refined, slightly reddish-yellow; it has characteristic but not very pronounced smell and taste. About 18 grams dissolve in 1000 c.c. of absolute alcohol at 15°. The other physical and chemical characters are indicated in Table XLIV.

Heydenreich's reagent gives a deep orange, and Hauchecorne's or Brullé's reagent a reddish-brown, coloration with the oil. The latter also gives the following characteristic reactions:

**1. Milliau's Reaction, modified by Armani.**—10 grams of the oil are saponified in the usual way, the soap being dissolved in water and the solution shaken in a separating funnel with 100 c.c. of ether and 30 c.c. of 10% hydrochloric acid. After standing, the acid aqueous layer is removed and the ethereal solution of the fatty acids washed by shaking several times with water until the latter no longer gives an acid reaction. The ether is then evaporated, the fatty acids thus obtained being dissolved in 15 c.c. of 90% alcohol (puriss.) [1] and the solution mixed with 1–2 c.c. of alcoholic silver nitrate solution and heated in a water-bath at 80–90°.

Pure cottonseed oil gives an intense brown coloration almost immediately and then also a black precipitate. Mixtures of oils or fats containing cottonseed oil yield a violet-brown coloration which, after a few minutes' heating,

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[1] This reaction and in general all reactions with silver nitrate require the use of

tion appears after 5–10 minutes of heating, whilst with
from cottonseed oil no sensible coloration is ever forme

**2. Milliau's Reaction, modified by Tortelli and**
liquid fatty acids are extracted from 20 grams of the oi
Ruggeri's lead-salt method (*see* General Methods, 18, 1) a
dissolved in a test-tube in 10 c.c. of 90% alcohol (puriss.),
thoroughly mixed with 1 c.c. of 5% aqueous silver nit
heated in a water-bath at 70–80°.

With pure cottonseed oil the liquid assumes almos
reddish coloration which soon turns to reddish-brown, the l
ing turbid and appearing violet-blue in transmitted lig
after 5–10 minutes heating. With oils and fats quite fre
oil no coloration is obtained even after heating for hal
mixtures containing only 1% of cottonseed oil, a deep b
appears.

**3. Halphen's Reaction.**—According to the most
by the author,[1] this test is carried out as follows: In a te
1 c.c. of the oil and 2 c.c. of sulphocarbon reage
dissolving 1 gram of powdered, refined sulphur in 100 c.c
phide and then diluting with 100 c.c. of amyl alcohol. Th
to the extent of two-thirds in a salt solution and heated
hour, 2 c.c. of the same reagent being then added and the
for 30–40 minutes. In presence of cottonseed oil, a red
pink coloration—according to the proportion of cotto
(down to about 1% as a minimum)—appears more or l

Water hinders the reaction, so that the test-tube should
and the reagents and oil anhydrous; the latter is filtered
dry filter.

Some cottonseed oils which have undergone special t
place of a decided red coloration, a brown tint with an oran
well seen by looking through the whole depth of the liquid

With green or greenish olive oils containing little cottons
is uncertain; in such cases it is well to decolorise the oil bef
it at about 50° with animal charcoal and filtering at the sam

**4. Halphen's Reaction, modified by Gastaldi.**—
taining 5 c.c. of the oil, 1 drop of pyridine and 4 c.c. o
sulphur in carbon disulphide is heated in a boiling wat
30–60 minutes. In presence of cottonseed oil a red, pin
coloration—according to the amount of the cottonseed
with Halphen's reagent; the colour is more distinct and
the latter and is visible even with 0·5% of cottonseed

is, however, of little practical value, since cottonseed oil treated in this way is scarcely utilisable, at any rate for mixing with comestible olive oil.

It is also to be noted that kapok and baobab oils give the same reactions as cottonseed oil, both with silver nitrate and with the carbon disulphide reagent, but even far more intensely (with silver nitrate the reaction occurs even in the cold and with Halphen's reagent, 1% of kapok oil mixed with other oil gives almost the same coloration as pure cottonseed oil). Kapok oil may, according to Milliau,[1] be distinguished from cottonseed oil by means of the action of silver nitrate on the fatty acids in the cold; but actually the fatty acids of cottonseed oil also slowly reduce silver nitrate in the cold and, in the case of mixtures, the reaction may be due as much to a little kapok oil as to a large amount of cottonseed oil. For a more certain indication other data must be employed. For instance, with mixtures of olive and arachis oils, the iodine number and other constants will show if the proportion of the extraneous oil is large or small. Thus, an arachis oil which gives Halphen's reaction as sharply and intensely as pure cottonseed oil but has a normal iodine number and a normal content of arachidic and lignoceric acids cannot possibly contain an amount of cottonseed oil capable of giving such an intense colour reaction; it is, therefore, more probable that such an oil is contaminated with a little kapok oil than with much cottonseed oil.

⁂

*Comestible cottonseed oil* should show little colour and no unpleasant smell or taste and no acidity. The *industrial oil* should have: D = 0·922–0·930, iodine number = 103–110, solidification point of the fatty acids = 32–40°, Maumené number (Tortelli) = 78·8°.

*Refinery residues of cottonseed oil* (*soapstock*), which are pasty and brownish-yellow to black, are valued on the basis of their total content of fatty matter (standard 50%), for the determination of which, *see* General Part, 1, *A–C*.

*Cottonseed margarine* or *stearine* is the solid part which separates on cooling the oil and is recovered from the latter by pressure at 10–11°; it is white or yellowish, has the consistency of butter (m.p. 16–32°) and gives the same colour reactions as cottonseed oil. Its specific gravity at 100° is 0·864–0·868, saponification number 194–195, iodine number 95–96. Its value depends on the titer (solidifying point of the fatty acids; *see* Tallow) and on the content of total fatty matter (*see* General Part, 1, *A–C*).

## LINSEED OIL

Ordinary or crude linseed oil (for boiled linseed oil, *see* next chapter: Industrial Products of the Treatment of Fatty Matters), from the seeds of *Linum usitatissimum*, is yellow or brownish-yellow and has a peculiar odour and an unpleasant taste. It dissolves in about 40 parts of cold or 5 parts of boiling absolute alcohol. It contains a certain quantity of unsaponifiable substances (1–1·3%). Its physical and chemical characters are given in Table XLIV.

**1. Reaction of the Hexabromo-compounds.**—
shaken in a stoppered cylinder with 100 c.c. of a mixture of
acetic acid, 4 vols. of nitrobenzene and 1 vol. of bromine (
*reagent*), 5 c.c. of the oil give a yellow precipitate compose
compounds of linolenic acid. This precipitate is soluble i
and melts undecomposed at 175–180° (difference from oils o
*see* Fish Oils).

Drying walnut and hempseed oils behave like linsee
vegetable and animal oils (excepting those of marine
precipitate or only a slight turbidity with the bromine

**2. Drying Properties.**—Linseed oil, being a drying oi
oxygen, its drying power increasing with the rapidity with
its maximum proportion of oxygen. Under the conditi
method (*see* General Methods, 22, Drying Properties of Oil
oil absorbs about 14% of oxygen in two days, while by
the maximum is 17% and is reached in 24 hours.

**3. Detection of Adulterations.**—Linseed oil may
with other vegetable oils (especially colza, cottonseed, se
cameline, hempseed and other drying oils) or with animal
oils, which are tested for as follows :

1. Other Vegetable Oils. Marked addition of oth
(especially if non-drying) to linseed oil generally lowers t
and the Maumené number and a linseed oil with an iodi
165 and a Maumené number less than 120° is to be su
ticular, colza oil may be detected by the Tortelli and Fo
seed oil by the Halphen and the silver nitrate reaction
by the furfural reaction (*see* these oils). The presence of d
seed, cameline and the like) is moderately difficult to asce
oils do not possess special colour reactions.

2. Fish and other Marine Animal Oils. The pres
may be detected by the Halphen and Marcusson octa
test and the Tortelli and Jaffe colour reaction (*see* Fish

3. Mineral Oils. These are detectable by the fact
the density, the iodine number and the saponification num
they may, in addition, be tested for in the unsaponifiable
Methods, 19, Unsaponifiable Substances).

4. Resin Oils. These may be recognised by the odo
reaction with sulphuric acid (*see* Resin Oils) and by th
(linseed oil is almost inactive, whereas resin oils are
rotatory) ; further, they increase the density and lowe

## ALMOND OIL

This is obtained from the seeds of *Amygdalus communis* or ordinary almonds, the sweet and bitter varieties giving oils very similar in all their properties. Almond oil is yellow or golden-yellow and about 16 grams of it dissolve in 1000 c.c. of absolute alcohol.

With Heydenreich's, Hauchecorne's and Brullé's reagents it remains pale yellow or becomes somewhat paler. The characters of the oil are given in Table XLIV and are determined by the methods already described.

**Detection of Adulterations.**—Almond oil may be adulterated with various seed oils (arachis, colza, cottonseed, walnut, sesamé, etc.), but especially with peach-kernel, apricot-kernel and plum-kernel oils. To detect such admixtures, the various characters must be determined (especially solidifying points of the oil and of the fatty acids, saponification and iodine numbers, Maumené number) and certain colour tests made (*see* below, 2).

The different extraneous oils may be detected as follows:

1. ARACHIS, SESAMÉ, COTTONSEED, COLZA, ETC. The first is detected by the arachidic and lignoceric acids, the second by the furfural reaction, the third by the Halphen reaction, and colza oil by tests on the fatty acids (*see* the respective oils). The presence of other seed oils in general (excluding those dealt with in 2) may be recognised by the colour reactions of Heydenreich, Hauchecorne, Brullé and Bellier (*see* General Methods, 23), to which almond oil does not sensibly respond.

2. PEACH-KERNEL, APRICOT-KERNEL AND PLUM-KERNEL OILS. These oils are commonly used as adulterants or substitutes for almond oil. They do not alter the characters of almond oil appreciably, excepting that apricot-kernel oil somewhat increases the Maumené number (50–51 for almond oil and 60–70° for apricot-kernel oil). The two following reactions serve for their detection.

*Bieber's reaction.* Equal volumes of pure sulphuric acid of 66° Baumé, concentrated nitric acid (D 1·42) and water are mixed, one vol. of such mixture being then shaken with 5 vols. of the oil in the cold. Pure almond oil forms a yellowish emulsion which becomes reddish only after some time. Apricot-, peach- and plum-kernel oils form emulsions of a transient purple colour, which soon changes to deep orange and then to brown.

*Reaction with nitric acid.* 1 c.c. of fuming nitric acid, 1 c.c. of water and 2 c.c. of the oil are shaken vigorously at a temperature of about 10°: pure almond oil yields a whitish emulsion which, in two or at most six hours, sets to a solid mass of compact white granules with a little colourless, supernatant liquid. In presence of apricot- or peach-kernel oil the emulsion becomes coloured almost immediately, more or less reddish

D = 0·914–0·920, iodine number = 94–100, saponification nu and should be incongealable at — 10° and should respond to th with nitric acid.

## OLIVE OIL

This is obtained from the fruit of *Olea europea*, and is sometimes greenish and with characteristic smell and ta grams of the oil dissolve in 1000 c.c. of absolute alcohol at

With Heydenreich's, Hauchecorne's, Brullé's or Belli gives a pale-yellow or greenish coloration, excepting with rancid oils, which yield more or less deep orange tints. Th the oil are given in Table XLIV.

Olive oil may be adulterated with various seed oils, arachis, cottonseed, sesamé, colza, ravison or soja-bean oil, an with maize, poppyseed and other oils. Adulteration with la mineral oils has been observed, but only in exceptional ca

1. **Tests and Determinations.**—Analysis of olive oil of ascertaining the quality and purity, includes mainly th

(*a*) Examination of the objective properties, that is, t pidity), colour, smell and taste. The odour is brought out a few drops of the oil between the hands and smelling t odour and taste indicate the fineness of an oil, its state of pr with much practice, its purity.

(*b*) Determinations: solidifying point of the oil and t solidifying points of its fatty acids; the specific gravity; on the Zeiss butyro-refractometer at 25°; the Maumené acid, saponification and iodine numbers. All these are made described in the general part of the present chapter (except refractometer reading, for which *see* Butter, Vol. II).

(*c*) Elaidin test (*see* General Methods, 24).

(*d*) The arachidic and lignoceric acid test and the Tort tests for erucic acid (*see* Arachis Oil and Colza Oil).

(*e*) The colour reactions of Heydenreich, Hauchecorne, Milliau, Halphen, and Villavecchia and Fabris (*see* Genera also Cottonseed Oil and Sesamé Oil).

(*f*) With industrial olive oils, determinations of the m traneous impurities are necessary (*see* General Methods, sometimes required to ascertain if the oil has been extract disulphide (*see* later, 8).

. **Detection of Extraneous Oils.**—The various fore ises the specific gravity, the melting and solidifying points of the fatty , the Maumené number, the refractometric value and the iodine number.

. SESAMÉ OIL : by the Villavecchia and Fabris reaction (*see* Sesamé ; it alters the different characters in the same sense as does cottonseed

. OTHER SEED OILS IN GENERAL : by the general colour reactions dy indicated (*see e*, above) and by certain alterations in the characters ie oil.

. ANIMAL OILS : by the smell and by testing for cholesterol as indicated llow (olive oil scarcely contains traces of phytosterol). Fish oils and of other marine animals are detected by the Tortelli and Jaffe reaction Fish Oils).

. MINERAL OILS : by the lowering of the saponification number and xamination of the unsaponifiable part (*see* General Methods, 19).

. **Detection of Sulphocarbon Oil.**—200 grams of the oil are rously shaken with 50 c.c. of 90% alcohol and distilled from a water- , the distillate being collected in a flask containing a few c.c. of alcoholic tic potash solution (1 : 10) (recently prepared from the purest alcohol) mmersed in cold water. When about two-thirds of the alcohol added ie oil are collected, the distillation is interrupted. The distillate is ly acidified with dilute acetic acid and treated with 1–2 drops of dilute er sulphate solution : in presence of potassium xanthate (formed by ction of the carbon disulphide, distilled with alcohol, on the alcoholic sh), a brown coloration is formed and then a yellow precipitate of er xanthate.[1] The presence of carbon disulphide in the oil is hence luded.

⁂

enuine *comestible olive oil* should have the following characters :

: should be clear and have the normal odour and taste.

*olidifying point* : it should begin to become turbid at about 10°, and as e it sets to a semi-solid mass between 6° and 2° ; at 0° it forms a soft solid.

*Ielting point of the fatty acids* : 22–28°.

*olidifying point of the fatty acids* : 24–21°.

*pecific gravity* at 15° : 0·914–0·919.

*eading on Zeiss butyro-refractometer* at 25° : 62–63. With oils which are tive or altered, or obtained from bad olives, or washed or extracted with on disulphide, the reading may be as low as 60.

*Iaumené number* (Tortelli) : 41–47° (44° may be taken as the mean). With Jean thermo-oleometer : 32–39°.

*cid number* : 2 at the most.

*aponification number* : 185–196 (normally 192–195).

*odine number* : 79–88. Most commonly the iodine number is 80–83, only n oils from Li uria and Spain, and more often the oils of Crete, Tunis, animal oils.

In general, an olive oil may be regarded as pure when : it i pale yellow by Heydenreich's, Hauchecorne's or Brullé's reagen fication number not less than 192 and an iodine number not ex does not contain arachidic, lignoceric or erucic acid. An oil cation number less than 192 and an iodine number above 83—w the limits indicated in Table XLIV—but of normal behaviou the other tests, may be regarded as genuine.

The official Italian methods give for olive oil the limits i for the different characters, excepting that the solidifying temp as 2–6°, the refractometer reading at 25° as between 62 and 62·8 number as 79–90. They give further : Reichert-Meissl numbe number, 95·5–96·2 ; acetyl number, 4–10 ; absolute iodine nu unsaponifiable residue, which should be constituted of mini phytosterol scarcely sufficient for the reaction with chloroform acid (100 grams of the oil yield 0·45–0·47 gram of crude phy sesamé and cottonseed oils give respectively 1·28 and 1·20 gr

The *industrial oil for lighting or lubrication* should answer th indicated for the genuine comestible oil. In some cases, howe of seed oils (arachis, colza or ravison) are allowed, e.g., by th Railways. It should not contain more than 1% of free acid monohydrated sulphuric acid), should not congeal above — 5°, adulterated with animal, mineral or resin oils, and should not laginous substances or suspended foreign matters. Further, nating purposes should satisfy definite requirements with rega of burning, the illuminating power, etc.

*Industrial olive oil for soap-making* occurs in various qualit

*Washed oil,* obtained by washing the olive residues (sanse) impurities up to 2% ; free from sulphur ; acidity variable (1 acid).

*Huile lampante* (yellow and green), obtained by filtering t moisture and impurities up to 1%.

*Olive oil grease* or residues from the filtration of the washed free from sulphur, unbleached and not treated with acid. Its on its content in total fatty matter—to be determined directly—c in fatty acids (exclusive of hydroxy-acids)—to be determined the grease and separating the total fatty acids.

*Sulphur or sulphocarbon olive oil,* which is distinguished f saponification number not less than 180, acidity (as oleic aci moisture and impurities up to 2% and hydroxy-acids up to 3

## CASTOR OIL

From the seeds of *Ricinus communis,* is almost colourles dense and viscous, with characteristic smell and taste. alcohol in all proportions and in acetic acid in the cold. almost insoluble in petroleum ether and in vaseline oil, whils stor oil is readily distinguished from other oils by its solubility in l and its insolubility in mineral oils, by its specific gravity, acetyl er, viscosity and rotatory power, which are considerably higher than ther oils. Its viscosity (Engler) at 50° is about 16 (water at 20 = 1) s rotation in a 20 cm. tube at the ordinary temperature + 8° to + 9° ar degrees).

en prepared recently and in the cold, it is neutral, but it easily becomes . Old oils and those extracted in the hot or by solvents are more or id (up to more than 20% of free acids, as oleic acid).

e following tests are usually made:

**Solubility.**—This serves to show if the oil is pure or not, and is l out as follows:

*Finkener's test.* 10 c.c. of the oil and 50 c.c. of 90% alcohol are together: if the mixture is turbid and remains so at 20°, the castor not pure.

*Morpurgo's test.* 1 vol. of the oil and 3 vols. of oil of vaseline are together at 10–15°: after standing, the oil of vaseline separates ts original volume if the castor oil is pure, but with an increased e if extraneous oils are present.

**Detection of Adulterations.**—(*a*) VARIOUS VEGETABLE OILS. oil is rarely adulterated with vegetable oils (cottonseed, sesamé, linseed, etc.), which may in any case be easily detected, since they the specific gravity, acetyl number and rotatory power and raise ponification number (excepting colza or ravison oil).

CROTON ELLIOTIANUS OIL. This oil does not greatly alter the ties and is difficult to detect, especially if only in small proportion. dication of its presence may, however, be obtained by boiling the h a very concentrated potassium hydroxide solution: on cooling, a soapy mass is obtained with pure castor oil, and a yellow or brown n presence of croton oil (1% or more).[1]

**Test for Resinous Substances.**—To ascertain if a sample of castor contaminated with resinous substances or has been *extracted in the* e following test, prescribed by the official Italian pharmacopœia, is 3 c.c. of the oil, 3 c.c. of carbon disulphide and 1 c.c. of conc. ric acid are shaken together for some minutes: the mixture should rn brown.

⁂

*dicinal castor oil,* according to the official Italian pharmacopœia, should racted by pressure in the cold from husked, peeled seeds; it should be almost colourless or yellowish, and not of acrid taste, soluble in 5 parts alcohol at 15° and in 2 parts at 25°, and extremely soluble in absolute

## TABLE XLIV

## Characters of Vegetable Oils[1]

| | Specific Gravity at 15°. | Solidifying Point. | Zeiss Butyro-refractometer Reading. | | Maumené Number (J=Jean, T=Tortelli apparatus). | Saponification Number. | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | t. | | | | | | | Melting Point. | Solidifying Point. |
| . . . . . . . . | 0·914–0·920 | —10 to —15° | 25° | 64–65 | 50–51 T | 187–196<br>(192 | 93–103<br>(95) | 96–97 | — | 12–15° | 5–11° |
| el . . . . . . | 0·915–0·921 | —14 to —20 | 25 | 65–67 | 60–61 T | 187–193 | 96–109<br>(100) | 95–96 | — | 2–7 | 0–4 |
| . . . . . . . . | 0·916–0·920 | —3 to —7 | 25 | 62–67 | 51–60 T | 185–197<br>(193) | 83–103<br>(92–95) | 95–96 | 1 | 27–33 | 22–32 |
| s (Andansonia) . | 0·915–0·919 | +3 to —3 | — | — | — | 190–192 | 76–79 | — | — | 35–38 | 32–34 |
| . . . . . . . . | 0·920–0·922 | —17 | — | — | 63–65 J | 191–196 | 104–111 | 95 | — | 23–24 | 17 |
| . . . . . . . .<br>*rigosperma Gaertn.)* | 0·912–0·919 | 0 | ? | 50–60 | — | 185–188 | 72–112<br>(80–84) | 95 | 0·5 | — | 37–38 |
| . . . . . . .<br>*excelsa H.B.)* | 0·917–0·919 | 0 to —4 | — | — | 50–52 J | 170–194 | 90–106 | — | — | 28–30 | 25–27 |
| rman sesamé oil) | 0·920–0·933 | —18 | — | — | 103 T | 188 | 132–153<br>(150) | — | — | 18–20 | 13–14 |
| Kekuna) . . .<br>*luccana, A. triloba* | 0·920–0·926 | —18 to —20 | ? | 76 | — | 179–195 | 136–164 | 90 | 1–3 | 18–21 | 13–15 |
| . . . . . . . . | 0·916 | — | 25 | 62 | — | 179–195 | 60–84 | — | — | — | — |
| . . . . . . . . | 0·960–0·973 | —10 to —18 | 25 | 78 | 74 T | 176–186<br>(180) | 82–91<br>(85) | — | 2–3 | 13 | 2–3 |
| vison . . . . . | 0·913–0·918 | —3 to —10 | 25 | 68–71 | 61–62 T | 167–180<br>(177) | 94–106<br>(100) | 95–96 | 0·5 | 17–24 | 12–18 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0·923–0·933 | —10 | 25 | 64–68 | 95 J | 16 –195 | 73–96 | 95 | 3–4 | 27– | 2–34 |
| | 0·925 | 0 | — | — | — | 182 | 92 | — | — | 32–35 | 27–30 |
| | 0·930–0·937 | —16 to —27 | 25 | 81–87 | 124–138 T | 187–195<br>(192) | 164–194<br>(170–190) | 95–96 | — | 17–24 | 13–20 |
| | 0·926–0·935 | —10 to —20 | — | — | 96–101 J | 192–193 | 117–120 | — | — | 23–26 | 20–22 |
| | 0·921–0·926 | —10 to —20 | 25 | 71–72 | 82 T | 188–198<br>(190) | 111–128<br>(120) | 92–95 | 0·3–4 | 18–23 | 14–16 |
| ive | 0·918–0·919 | — | — | — | — | 192 | 94–96 | — | 1–2 | — | — |
| *ideroxylon*)<br>d, black | 0·915–0·920 | —17 | 25 | 69 | 74–77 T | 174–182 | 96–122 | 95–97 | — | 16–17 | 15 |
| edge) | 0·917 | —8 | — | — | — | 174 | 105 | — | — | 12–13 | — |
| an | 0·916–0·920 | — | 40 | 60 | — | 172–180 | 102–108 | 95–96 | 0·3–1 | — | — |
| te | 0·913–0·920 | 16 | 40 | 85–86 | 58–59 T | 170–176 | 92–103 | 96 | — | 15–16 | 12–14 |
| Guizotia) | 0·923–0·928 | —7 to —13 | 40 | 63 | 91–96 T | 189–192 | 126–134 | 94 | 0·5 | 29–33 | 28–30 |
| | 0·913–0·919<br>(0·916–0·918) | 0 to 6 | 25 | 62–63 | 41–47 T<br>(44) | 185–196<br>(192–195) | 79–88<br>(80–83) | 95–96 | 0·3 | 22–28 | 21–24 |
| l | 0·918–0·923 | —20 to —23 | 25 | 63–67 | 51–53 T | 189–192 | 94–96 | — | — | 5–14 | 4–7 |
| | 0·930 | — | — | — | — | 189–190 | 206 | — | — | 5 | — |
| it | 0·918 | —10 to —11 | 25 | 62 | 55 T | 191–192 | 86–93 | 96 | — | 17–20 | 13–14 |
| l | 0·912–0·919 | —5 to —10 | 25 | 63–64 | 44–45 T | 189–192 | 91–101 | 96 | — | 11–21 | 7–15 |
| | 0·924–0·937 | —18 | 25 | 71–74 | 88–89 T | 190–198<br>(193) | 131–157<br>(137) | 94–96 | 0 | 20–21 | 15–17 |
| | 0·914–0·918 | —15 | 40 | 57–58 | 51–52 J | 173–179 | 93–112 | 96 | 0·3 | 20 | 13–15 |
| | 0·907–0·923 | —10 | 25 | 68–69 | 67 T | 181–198 | 91–108 | 95–96 | 1 | 31–36 | 28–29 |
| d | 0·922–0·930 | —21 | — | — | — | 191–206 | 117–141 | 95 | 0–3 | — | 15 |
| | 0·928–0·938 | —13 to —20 | 25 | 77–78 | 101–120 T | 186–195 | 126–150<br>(140) | 91–95 | 1–2 | 11–17 | 7–12 |
| | 0·922–0·926 | —5 | 25 | 66–70 | 71 T | 187–193<br>(190–192) | 102–116<br>(108) | 95–96 | 1 | 25–35<br>(27–30) | 23–32<br>(23–25) |
| | 0·924–0·929 | —10 to —15 | 25 | 73–74 | 83 T | 182–193<br>(185) | 115–137<br>(133–135) | 94–96 | 0·1 | 20–29<br>(24–25) | 16–25<br>(20–21) |
| | 0·939–0·943 | below 0 | 25 | 86 | 136–138 | 204–210 | 145–161 | 94–96 | 1 | 14–15 | 12–13 |
| | 0·923–0·936 | —16 to —18 | 25 | 72–73 | 88 T | 188–194 | 120–137<br>(133) | 95 | — | 17–24 | 17–18 |
| ed | 0·920–0·924 | —20 | 25 | 71–72 | — | 183–191 | 106–118 | 95–96 | 2 | 26–29 | — |
| | 0·925–0·926 | —15 to —27 | 40 | 65–68 | 104 T | 188–197<br>(194) | 143–152<br>(148) | 95–96 | 0 | 16–20 | 13–16 |
| m) | 0·924–0·929 | —15 | — | — | — | 182–190 | 115–123 | — | — | 30–40 | 29–30 |

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[1] The numbers in brackets indicate the more common limits or mean values.

*Castor oil for industrial purposes* (soap-making) may hav impurities up to 1%; D = 0·960–0·974; iodine number, 8 point, — 10° to — 18°; solidifying point of the fatty acids = 3 of the fatty acids = 153·4–156; Maumené number (Tortelli

## SESAMÉ OIL

From the seeds of *Sesamum indicum* and *S. orientale* deep yellow, of faint special odour and pleasant taste. grams dissolve in 1000 c.c. of absolute alcohol at 15°. I given in Table XLIV.

With Heydenreich's, Hauchecorne's, Brullé's and Bel gives the colorations usual for seed oils. Characteristic the following colour reaction, which serves to detect it in all other oils and fats.

**1. Villavecchia and Fabris Reaction.**[1]—Two or thr holic furfural solution (2 grams of furfural in 100 c.c. o and then 5–10 c.c. of the oil and 10 c.c. of pure conc. l (D 1·19) are poured into a test-tube, the whole being well moments and then left to stand. The acid, coloured dark ro in the lower part of the tube and becomes increasingly dark oily layer represents a yellowish-red emulsion. The colo observable even with mixtures containing only 0·5% of

No other oil gives such a reaction; only certain olive oils Algeria, and some from Bari, Brindisi and Lecce) may yiel reagent a pink or reddish colour, which is, however, always and *quite different* in tint from that produced by sesamé oil. the reaction may be carried out with the liquid fatty acids sep and Ruggeri's method (*see* General Methods, 18, 1).

**2. Detection of Adulterations.**—Sesamé oil may be drying oils, colza oil and arachis oil: the first raise the io the Maumené number, while the others are detectable by arachidic and lignoceric acids and by the Tortelli and Arachis Oil and Colza Oil).

⁂

*Comestible sesamé oil* should be clear, of normal taste an too acid (fresh oil may contain 0·5–5% of free acids, calcula old oils may contain as much as 35%).

The permissible limits for the *industrial oil* (for soap-makin ené number (Tortelli) = 71·3°; solidifying point of the fatty acids = 4°.

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[1] This reaction (see *Zeitschr. für angew. Chemie*, 1892, p. 509, a

# Vegetable Fats

ese are fatty substances of vegetable origin and solid at the ordinary rature. Among them are also some so-called *Vegetable waxes*, such an wax and myrtle wax, which are, however, not true waxes but solid nce they are composed of glyceryl esters and not esters of higher s.[1] True waxes of vegetable origin include only carnauba wax and others (*see* Waxes).

e more important vegetable fats are those of cacao, coco-nut, palm alm-kernel, vegetable tallow and a few others which are described; characters are given in Table XLV, together with those of other ble fats of some interest.

## CACAO BUTTER

## (Cocoa Butter)

om the seeds of *Theobroma cacao*, is a somewhat brittle, yellowish- solid with a taste and smell recalling those of torrefied cacao. It es in 5 parts of boiling absolute alcohol and is almost insoluble in lcohol; it is soluble in 3 parts of ether. It does not readily turn , and only when very old or badly stored does it contain more than free acid (calculated as oleic acid); the rancid fat is white. Fat e skins of cacao seeds is, however, markedly acid even when fresh. aracters of the fat are given in Table XLV.

**tection of Adulterations.**—It may be adulterated with coco-nut , tallow, stearine, solid paraffin and wax, or, more rarely, with other ble fats (Japan wax, Dika oil), almond oil, hazelnut oil or other seed Such adulterations are detected by determining the different char- of the fat, bearing in mind the following:

o-nut oil raises the saponification number and the volatile acid r, but lowers the iodine number and the refractometric reading. e raises the acid number and lowers the iodine number, and is, more- asily detectable by its ready solubility in alcohol. Solid paraffin ax lower the saponification number and the iodine number and may gnised in the unsaponifiable portion. Vegetable oils in general lower ecific gravity and the melting point and raise the iodine number and fractometric reading. Japan wax increases the density, the acid d the saponification number and lowers the iodine number. Dika

## TABLE XLV

## Characters of Vegetable Fats[1]

| | Specific Gravity. | | Melting Point. | Solidifying Point. | Zeiss Butyro-refractometer Reading. | | Saponification Number. | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty Acids. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | t. | | | | t. | | | | | | Melting Point. | Solidifying Point. | Acetyl Number. |
| ang fat)<br>*pus* | 100° | 0·854–0·856 | 34–43° | 22–27° | 40° | 45–46 | 191–196 | 29–30 | 95–96 | — | 54–55° | 48–54° | — |
| . . | 15<br>100 | 0·940–0·976<br>(0·950)<br>0·857–0·858 | 26–36<br>(30–35) | 20–27 | 40 | 46–48 | 192–204<br>(195) | 28–42<br>(35–40) | 94–95 | 1–4 | 48–53 | 45–51 | 3 |
| ulou-<br>. .<br>*eet*) | 15 | 0·912–0·923 | 23–31 | 18–26 | — | — | 195–196 | 65–72 | 93–94 | 4–5 | 36 | 32–33 | — |
| diroba<br>. .<br>*bl.*)[2] | — | — | liquid | — | — | — | — | — | — | — | — | 36 | — |
| . . | 40 | 0·917–0·921 | 15–20 | 8–10 | — | — | 198–202 | 72–84 | — | 3–4 | — | 35–39 | — |
| . . | 15<br>100 | 0·925<br>0·863–0·874 | 20–28 | 14–26 | 40 | 33–36 | 246–268<br>(260) | 8–10 | 83–92 | 7–9 | 21–27 | 16–20 | — |
| ba oil)<br>) | 15<br>100 | 0·910<br>0·820 | 30–42 | 27–35 | — | — | 244–245 | 5 | — | 0·4 | — | 3–5 | — |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| . . *bcord.* | 100 | 0·857 | 35–45 | 25–37 | — | — | 198–221 | 40–47 | 93 | 1–4 | 51–55 | 44–52 | — |
| llow)[4]<br>.) | 15<br>100 | 0·917<br>0·897–0·898 | 25–42 | 20–36 | 40 | 52 | 190–200 | 60–68 | 94–95 | 1–2 | 39–45 | 38–41 | — |
| . . | 15<br>100 | 0·995–1·000<br>0·875–0·878 | 40–48 | 39–45 | 40 | 55 | 205–217 | 10–11 | — | — | 47–48 | 46 | — |
| ter) . | 40 | 0·898 | 44–47 | 38–40 | 40 | 52 | 182–190 | 56–59 | 94–96 | 1–3 | 46–51 | 43–47 | 13 |
| tter) .<br>*ult*) | 15<br>100 | 0·945–0·996<br>0·884–0·898 | 25–51<br>(25–30) | 24–44 | 40 | 48–85 | 154–191 | 31–81 | — | 1–4 | 40–49 | 39–45 | — |
| . . | 15<br>100 | 0·945–0·947<br>0·858–0·860 | 30–43 | 26–40 | 40 | 47 | 195–207 | 34–58 | 95–98 | 1 | 44–50 | 40–49 | 18 |
| . . | 15<br>100 | 0·952–0·955<br>0·867–0·873 | 23–30 | 20–27 | 40 | 36–37 | 241–260 | 10–20 | 87–92 | 4–7 | 20–28 | 20–25 | 2–9 |
| Karité<br>. . | 15<br>100 | 0·953–0·955<br>0·859–0·896 | 23–31 | 17–27 | — | — | 177–187 | 49–67 | 94–95 | 1–2 | 39–56 | 38–54 | — |
| etable]<br>. . | — | — | 47–52 | 45–50 | 50 | 38 | 205–231 | 16–19 | — | — | 55–57 | 53–54 | — |
| vege-<br>) . . | 15<br>100 | 0·918–0·922<br>0·860 | 36–47 | 27–34 | 40 | 44–45 | 196–207 | 28–100<br>(30–45) | 95–96 | 1 | 53–57 | 52–55 | — |
| . . | 20 | 0·912 | 39–43 | 32–33 | — | — | 219–220 | 9–10 | 93–94 | — | 42–46 | — | — |
| Piney)<br>. . | 15<br>100 | 0·915<br>0·890 | 36–42 | 30–40 | 40 | 42–47 | 188–192 | 30–45 | 95 | 0·3 | 56–57 | 54–55 | — |
| . . | 50 | 0·896–0·900 | 41–47 | 38–45 | — | — | 221–244 | 12–14 | — | — | 38–43 | 36–39 | — |

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n brackets indicate the more usual limits or mean values.

[2] Dextro-rotatory.

[3] Dextro-rotatory: $[\alpha]_D$ = 52–57°.

[4] Dextro-rotatory: $[\alpha]_D$ = about

and in glacial acetic acid and of the melting points of gly
in a mixture of alcohol and ether, as suggested by Grin

⁂

Cacao butter is to be regarded as genuine when its phys
characters lie within the limits indicated in Table XLV and it
any of the above-mentioned impurities.

It should be noted that *substitutes for cacao butter* are so
names, e.g., *chocolate butter*, consisting of coco-nut oil ; *caca*
oil and Japan wax). The so-called *Samana cacao butter* is a
at about 12° and when left for a long time separates a liqui
at 17·5° = 0·906, refractometric reading at 40° = 50·5 and
= 53–59.

## COCO-NUT OIL

From the albumin or pulp of the coco-nut, fruit of *Coco*
white or pale yellow, and has the consistency of butter and
In coco-nut butter well refined for comestible use this odour
lacking, but boiling with a little alcohol and a few drops o
acid brings out the odour distinctly.

It dissolves in 2 vols. of absolute alcohol at 30° an
90% alcohol at 60°. Its physical and chemical charact
Table XLV.

With Heydenreich's, Hauchecorne's or Brullé's reag
sensible coloration, and it does not react with silver nitrate
and hydrochloric acid. Characteristic of coco-nut oil are
saponification number, the low iodine number and the vola
which is greater than those of vegetable oils and fats in

⁂

*Pure, edible coco-nut oil* is perfectly white (sometimes d
imitate butter), odourless and neutral or almost so (acidity nu
1% as oleic acid) and has a fresh, pleasant taste.

*Industrial coco-nut oil* (for soap) is white or faintly yellow
or less pronounced taste and smell. The finest and whitest
name *Cochin neige*, while the others are called *White Cochin,*
*oils.*

The allowable limits for these industrial oils are : acidi
up to 4% for Cochin and up to 10% for other qualities ; mo
impurities, up to 1% ; m.pt. = 20–28°, setting point = 22–1
point of the fatty acids) = 16–23° ; volatile acid number =
fication number = 248–260 ; iodine number = 7·68–9·5.

## P LM OIL

esterol (*see* General Methods, 19).

value depends essentially on the content of moisture and foreign
ties and on the setting point of the fatty acids (titer). These, then,
principal determinations made (*see* General Methods, 1, and also
) ; the acid saponification number is also measured and sometimes
cerine content (*see* General Methods).

⁂

titer of palm oil generally lies between 40° and 50°. Its content of
d foreign matters varies from 0·5% to 17%, but with a good specimen
not exceed 2%. Commercial palm oil is always markedly acid ; when
prepared the oil may contain about 10% of free acids (calculated as
acid), but most commercial oils show 20–50%, while certain old oils
al type may contain nearly 90%. As a rule the content of glycerine
hes as the free acid increases.

best commercial oil is that from *Lagos*, with 2% of moisture and im-
at most ; minimum titer, 43° ; acidity usually not greater than 20% ;
cation number, 196–207. The *Benin* oil, which is brown, has the titer
and acidity up to 50%.

## PALM-KERNEL OIL

m the seeds of the oil-palm (*Elaeis guineensis* and *E. melanococca*).
the consistency of butter, is white or yellowish, has a special odour
to that of coco-nut oil and readily becomes rancid. In all its pro-
it closely resembles coco-nut oil (*see* Table XLV), from which it is
to distinguish it. Analysis of this oil is carried out like that of
it oil (*q.v.*).

⁂

palm-kernel oil for industrial purposes up to 1% of moisture and ex-
s impurities are allowed and up to 10% of free acids ; saponification
= 241–250 ; volatile acid number = 4·8–5·6 ; titer = 20·5–25·5°.

## OTHER VEGETABLE FATS

the other vegetable fats the following are commonly known and used :

**getable Tallow or Chinese Tallow** (*Stillingia fat*), from the seeds
*lingia sebifera*. Its characters and properties may vary with the
of extraction, but it is usually solid, hard and white outside and
r less stained with earthy and vegetable residues, yellowish inside,
ourless, or almost so.

**pé-nut Butter, Fat or Oil** (*Mahwa fat*), from the seeds of *Bassia* origin (*see* Table XLV).

## Animal Fats

The most important animal fats are : butter, dealt witl on milk and its products (*see* Vol. II, Chapter II), tallow and the foot-oils, which are considered below in detail ; of other fats are obtained from different animals, but few ar The characters of these are given in Table XLVII.

So-called *wool fat*, which from its composition is to b wax, is dealt with in the article on waxes.

### TALLOW

This is a fat obtained from bovine (ox-tallow) and fror (sheep's or goat's fat). It is stiff and yellowish and has smell ; in the light and air it rapidly becomes rancid and d part of it dissolves in 40 parts of 94% alcohol. Its physic characters are given in Table XLVII.

Its analysis includes firstly the determination of the t point of the fatty acids), on which depends the commerci Determinations are also to be made of the water and fo of the acid and saponification numbers and, sometimes, (*see* General Methods). Any adulteration with bone fat, w or coco-nut oil, may be detected as described below (2).

**1. Titer Test.**—The sample for this determination carefully, portions being taken from each cake or cask (at of the bulk and these melted together at a temperature n and the fused mass continually stirred until it reaches th perature.

50 grams of this sample are saponified with 40 c.c. o solution (D 1·4) and 40 c.c. of 96% alcohol. The soap i litre of water and boiled in a dish to expel the alcohol, the f then separated by means of a slight excess of dilute sulphu boiling continued until these acids form a perfectly limpid suspended clots. The aqueous liquid is siphoned off and t with hot water until they no longer give an acid reaction wit and then solidified by cooling. The disc of solid acids is water-bath, filtered through a dry filter in a boiling wat filtrate left overnight in a desiccator.

The setting point of the fatty acids thus obtained i c tube and in the mass of the liquid. When rous crystals appear throughout the liquid, the is stirred gently with the thermometer until it nes pasty and opalescent and prevents the bulb e thermometer from being seen (stirring for 12-conds usually suffices); it is then left at rest.

efore and during the stirring the column of the ometer is carefully observed. It falls at first and regularly, but at a certain point the fall ns, then stops, and towards the end of the ion gives way to a rise to a maximum, the persisting for about two minutes. This station-emperature represents the solidifying point (titer) fatty acids examined.[1]

e result is controlled by re melting—after some (preferably 12 hours)—the fatty acids at a tem-ure not more than 5° above the solidifying point and allowing the molten mass to solidify in the conditions as before.

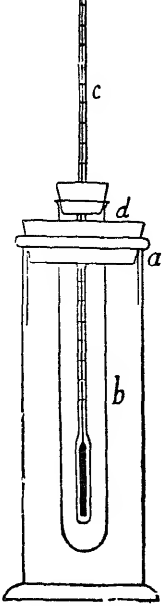

FIG. 58

hen the titer of a tallow is known, its yields of acids (oleic) and solid acids (stearic and pal- may be deduced from *Dalican's Table* (XLVI), which has been iled empirically by mixing a typical commercial stearine with fying point 54·4° with oleic acid freed from solid acids by pro- d standing and filtration. It indicates the percentages of stearic leic acids in a tallow, a deduction of 4% having been made for the ine and 1% for moisture and impurities.

c percentage of stearic or oleic acid in a mixture of fatty acids is by the formula

$$\frac{a \times 100}{95},$$

$a$ is the percentage of stearic or oleic acid given in Dalican's table.

**Detection of Adulterations.**—(*a*) Bone and wool fats: by the . They lower the saponification number (especially wool fat) and unsaponifiable matter is extracted, this contains a considerable amount lesterol (*see* General Methods, 19).

) Palm oil and coco-nut oil; by the odour; they raise the saponifi- number, and the latter oil lowers the iodine number.

---

[1] In place of the arrangement indicated above, Shukoff uses a vacuum-jacketed into which 30–40 grams of the fused acid are poured. The vessel is then

TABLE XLVI

| Solidification Point. | Stearic Acid % | Oleic Acid % | Solidification Point. | Stearic Aci % |
|---|---|---|---|---|
| 35° | 25·20 | 69·80 | 44·5° | 49·40 |
| 35·5 | 26·40 | 68·60 | 45 | 51·30 |
| 36 | 27·30 | 67·70 | 45·5 | 52·25 |
| 36·5 | 28·75 | 66·25 | 46 | 53·20 |
| 37 | 29·80 | 65·20 | 46·5 | 55·10 |
| 37·5 | 30·60 | 64·40 | 47 | 57·95 |
| 38 | 31·25 | 63·75 | 47·5 | 58·90 |
| 38·5 | 32·15 | 62·85 | 48 | 61·75 |
| 39 | 33·45 | 61·55 | 48·5 | 66·50 |
| 39·5 | 34·20 | 60·80 | 49 | 71·25 |
| 40 | 35·15 | 59·85 | 49·5 | 72·20 |
| 40·5 | 36·10 | 58·90 | 50 | 75·05 |
| 41 | 38·00 | 57·00 | 50·5 | 77·10 |
| 41·5 | 38·95 | 56·05 | 51 | 79·50 |
| 42 | 39·90 | 55·10 | 51·5 | 81·90 |
| 42·5 | 42·75 | 52·25 | 52 | 84·00 |
| 43 | 43·70 | 51·30 | 52·5 | 88·30 |
| 43·5 | 44·65 | 50·35 | 53 | 92·10 |
| 44 | 47·50 | 47·50 | | |

(*c*) Other vegetable oils: by the increase in the iodi
colour reactions, and by testing for phytosterol (*see* Hog's

(*d*) Cottonseed stearine: by Halphen's reagent (*see* Co

(*e*) Mineral substances (gypsum, talc and the like):
portion insoluble in ether.

⁂

Pure tallows of good quality give about 95% of fatty acids
44°, the commercial valuation being made with 43·5° as basis
tion number is 195–200. They give a mean of about 9·5%

According to the Union of Italian Soap-makers, the titer of
not be below 43·5°, while that of mutton-tallow may vary fr
In different varieties the acidity allowed varies from 3% to
and impurities allowed up to 1%.

## OLEOMARGARINE

This is the semi-fluid part expressed from tallow at abo

| | |
|---|---|
| pecific gravity at 15° | 0·924–0·930 |
| ,, ,, ,, 98–100° | 0·859–0·863 |
| lelting point | 32–35° (sometimes up to 40°) |
| ,, ,, of fatty acids | 40–43° |
| olidifying point of fatty acids | 39–42° |
| eiss refractometric reading, at 35° | 50–52° |
| ,, ,, ,, ,, 40° | 47–49° |
| cid number, if fresh and well stored | 0 |
| aponification number | 192–200 (195–198) |
| odine number | 42–55 (43–48) |
| ixed acid number | 95–96 |
| olatile ,, ,, | 0·4–1·0 |

der the polarising microscope it behaves like fused butter (*see* 3 in article tter, Vol. II, Chapter II).

## HOG'S FAT

og's fat is, strictly speaking, the fat of the inside of the animal, that ing to the inside of the skin constituting *lard*.

nerican hog's fat is divided into various qualities according to the od of preparation.

eneral the fat is white and pasty, with a peculiar odour and a sweetish , it becomes rancid easily, turning yellow. It is only slightly soluble cohol. With the ordinary reagents for oils it gives no colour reactions. aracters are given in Table XLVII.

**etection of Adulterations.**—Lard is adulterated with or even replaced xtures of tallow, pressed tallow (also hardened or hydrogenised oils), nseed stearine or other vegetable fats, or cottonseed, sesamé, arachis, , sunflower-seed, coco-nut or lard oil ; also with pressed lard and able oils. The artificial mixtures constituting *lard substitutes* often n a small proportion of lard, recognisable mainly by its characteristic . Lards containing marked amounts of water, incorporated with elp of a little alkali, are also found.

e various adulterations are detected as follows :

WATER, ALKALI AND OTHER MINERAL SUBSTANCES. The water is nined by drying the fat at 100° to constant weight. Alkalis and mineral matters may be found by incinerating the fat and examining h ; the former may also be detected by treating with hot water and g with litmus paper, or by passing a current of steam for half an hour mixture of 60 grams of the fat with 60 grams of water, then allowing ess to cool and filtering ; in presence of an alkali or an alkaline earth,

(a) *Preparation of the glycerides.* In a beaker of about 1 50 grams of the fused and filtered fat are dissolved in 50 c beaker being covered with a clock-glass, cooled to 15° an shaking, allowed to crystallise. After an hour the mass is a funnel containing a perforated disc covered with a lay pulp, the liquid being pumped off and the crystalline mass l then pressed with a watch-glass to free it from mother-liquo then dissolved again in 50 c.c. of ether and after an hour filte

The melting point of the glycerides thus obtained is for pure lard, but lower if tallow is present. If the meltin 61°, the glycerides must be recrystallised from ether in the n until a portion melting at least as high as 61° is obtained. certainty, it is necessary that the glycerides melt between

To obtain a good crystallisation of the solid glyceride soft fats rich in liquid glycerides, the ethereal solution s to 5–10°, or use made either of a mixture of 3–4 parts of e of alcohol, or of anhydrous acetone.

(b) *Preparation of the fatty acids.* From 0·1 to 0·2 gram m.p. 61–65°, is finely subdivided and placed in a beaker wit seminormal colourless alcoholic solution of potassium liquid is boiled carefully for 5–10 minutes to bring abou the soap being dissolved in 100 c.c. of water and the solu to a separating funnel, decomposed with 2–3 c.c. of 25 acid and extracted with 25 c.c. of ether. The filtered et evaporated and the residue dried at about 100° for 30–60 m cold, finely powdered.

(c) *Determination of the melting points.* The meltin glycerides and of the fatty acids prepared according to (*a*) determined under identical conditions. For this purpose perfectly similar U-tubes are used. With the help of a pl finely powdered substance is introduced into one of the lim so as to form a layer 2–3 mm. deep. The two tubes are a thermometer so that the branches containing the subst the bulb and the whole heated in a water-bath; when a 50° is reached, the heating is adjusted so that the rise in only 1·5–2° per minute. The temperature at which th liquid, clear and transparent is taken as the melting po mination should be repeated with fresh substance and t concordant results taken.

With pure hog's fat the difference (*d*) between the n

| G. | *d* | M.G. | *d* | M.G. | *d* |
|---|---|---|---|---|---|
| ·0° | 5·00° | 62·5° | 4·25° | 64·0° | 3·50° |
| ·5 | 4·75 | 63·0 | 4·00 | 64·5 | 3·25 |
| ·0 | 4·50 | 63·5 | 3·75 | 65·0 | 3·00 |

r each 0·1° variation in M.G. the difference $d$ changes by 0·05°, and um $\text{M.G.} + 2d$ is never less than 71 with pure hog's fat. Hog's fat ning tallow of whatever origin or pressed tallow or hardened oil lower value of $d$ than is shown in the above table, while $\text{M.G.} + 2d$ than 71.

AMPLES: A hog's fat gave: M.G. = 63·5° and M.A. = 58°, so that 5 and $\text{M.G.} + 2d = 74{\cdot}5°$; the fat is thus pure.

other fat gave: M.G. = 63° and M.A. = 60·5°, so that $d = 2{\cdot}5°$ and $2d = 68$. This fat contains tallow (pressed tallow, hardened oil).

VEGETABLE OILS AND FATS. COTTONSEED STEARINE. These adul- s are detected as follows:

*Colour reactions.* Bellier's reaction (*see* General Methods, 23, 4) the presence of seed oils in general; Villavecchia and Fabris' reaction f sesamé oil (*q.v.*); Halphen's reaction and the silver nitrate reaction ing to Armani or Tortelli and Ruggeri, that of cottonseed stearine ottonseed Oil).

achis oil is detected by the reaction for arachidic and lignoceric acids rachis Oil).

*Various characters.* Determinations are also made of the saponifi- , volatile acid and Polenske numbers (*see* General Methods, 8 and his chapter, and Butter, Vol. II), which detect the presence of coco- ; of the ordinary and absolute iodine numbers (*see* General Methods, l 13), which serve to confirm the presence of seed oils and to give an ximate indication of their quantity (when the nature of the vegetable s been ascertained); and of the rotatory power, for the detection of ocarpus (Maratti) and Mowrah fats (*see* later, d).

subsidiary determinations, measurements may also be made of the efractometric reading at 40° (*see* Butter) and of the Maumené number eneral Methods, 21).

*Detection of phytosterol.* This is of special importance in the analysis , since only with its help can it be decided if vegetable oils have really dded.

e all other animal fats and oils, hog's fat contains, as unsaponifiable

The united alcoholic liquids, which contain the unsaponifi
are boiled with 15 c.c. of 30% sodium hydroxide solution
tion is complete, the liquid being evaporated almost to d
residue extracted with ether. The ethereal solution is ev
ness and the residue left taken up in a little ether, filt
evaporated. The final residue is dissolved in a little boili
containing a few drops of dilute acetic acid and crystall

Repetition of the crystallisation from a little boiling
yields the *sterols* (cholesterol and phytosterol) ready for mi
nation. With practice and by comparisons of mixtures
position, the crystalline form observed under the micros
the cholesterol is pure or mixed with phytosterol; the ch
of the latter is evident in mixtures containing only 5% of
figures given under General Methods, 19).

The acetyl compound is then prepared as follows:
together with the last mother-liquor, are freed from alcoh
a glass dish on a water-bath, the residue being boiled fo
3–5 c.c. of acetic anhydride, the dish being covered with a
while; the cover is then removed and the solution evapo
on a water-bath. The residue is dissolved in boiling absolu
20 c.c.) and the solution left to crystallise at the ordin
When about two-thirds of the alcohol have evaporated,
collected in a small filter and washed with 2–3 c.c. of 95%
being then dried by pressing between filter-paper and t
solved in 5–10 c.c. of boiling absolute alcohol and left to
operation is repeated three times. After the third cr
melting point of the crystals is determined, two furthe
followed by determinations of the melting point being carri

(2) *Digitonin method*[2]: 50 grams of the fat are di
120 c.c. of chloroform and the liquid heated on the wat
60° with 20 c.c. of a 1% solution of digitonin in 96% alcoh
shaking; it is then left at rest overnight. The cholestero
combine with the digitonin forming insoluble products (*d*
are deposited at the bottom of the chloroform solution
liquid is filtered and the precipitate washed on the filter
and dried in the air.

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[1] *Zeitschr. für öffentl. Chem.*, 1897, p. 10.

[2] This method may be applied under the conditions laid dow
Schilling (*Chem. Zeit.*, 1913, p. 1001) or by Klostermann, Fritzsc
and Opitz (*Zeitschr. Unt. Nahr. Genussmittel*, 1913, XXVI, pp.

cetyl-compound thus obtained determined after the second, third or h crystallisation.

*elting point of the acetyl-compound.* This is determined in a very glass U-tube, into one branch of which the powdered substance is duced to form a layer 2–3 mm. deep. The observed melting point en corrected by means of the formula,

$$x = \mathrm{T} + [n(\mathrm{T} - t) \times 0{\cdot}000154],$$

e $x$ = correct melting point,

T = observed melting point,

$n$ = length of mercury column of thermometer protruding from the , expressed in degrees,[1]

$t$ = mean temperature of the air about the protruding part of the mometer, determined with another thermometer placed near the first with its bulb at the middle of the protruding portion of the stem.[2]

he *corrected* melting point of cholesterol acetate is 114·3–114·8°, whilst of phytosterol acetate is above 125°.

d) *Rotatory power.* This is determined on the fat as such or on the ponifiable substances extracted from it. In the former case, which es for the detection of Hydnocarpus oil, the rotatory power of the fat etermined in benzene solution at a temperature of about 20° with an nary shadow polarimeter. From the observed rotation the specific ion $[\alpha]_D^{20}$ is calculated by means of the formula,

$$[\alpha]_D^{20} = \frac{100\alpha}{lc}$$

re $\alpha$ is the observed angle in circular degrees, $l$ the length in decimetres he tube used, and $c$ the concentration, i.e., the number of grams of sub- ce in 100 c.c. of the solution.

The determination of the rotatory power of the unsaponifiable substance fected in the manner indicated by Berg and Angerhausen for the detec- of Mowrah butter in lard.[3]

⁂

Genuine hog's fat should not contain appreciable quantities of water, alkaline stances or other mineral matters, and should be free from all extraneous and oils.

Its physical and chemical characters should lie within the limits given in le XLVII. A saponification number above 200, volatile acid and Polenske bers higher than 1, and an iodine number below 45 demonstrate the presence

---

[1] For instance, if the thermometer is immersed up to + 5° and the observed melting

cottonseed, sesame or other seed cake. In such cases, adulti
the lard is proved only when the presence of phytosterol is
the case when the acetyl-compound of the sterols obtained as
has a corrected melting point higher than 115°.

Lard which gives the colour reactions but does not con
cannot be regarded as containing vegetable oil.

The melting point difference, determined by Bömer's me
such that the value of M.G. + $2d$ is 71 or more ; if this valu
the lard is considered adulterated with tallow, pressed tallow

In general, the following conclusions, based on the melting
and the phytosterol test, may be drawn [1]:

I. The melting point difference is normal : the lard is eith
terated with vegetable oils. The phytosterol test (m.pt. of
pound of the sterols) will demonstrate the presence or absence

II. The melting point difference is below the normal (M.G
71) : the following cases present themselves :—

1. Phytosterol test negative : lard contains tallow, hard
or both.

2. Phytosterol test positive : there may be—

(*a*) Addition of vegetable oils or hardened oils ;
(*b*) ,, of tallow (or pressed tallow) and vegetable
(*c*) ,, ,, ,, ,, ,, hardened

## BONE FAT

This is obtained by de-fatting bones by means of water,
(benzine, carbon disulphide). It varies in consistency but
and granular, and it has a yellowish or brown colour and a
It is somewhat soluble in alcohol, especially when it cont
acid. The physical and chemical characters vary somewh
the fat is pure or has been extracted with solvents or steam ;
in Table XLVII.

Bone fat contains cholesterol and, in accordance with
extraction, it may contain various impurities, such as wa
gelatinous substances and hydrocarbons.

The analysis of bone fat for the purpose of determining
value, includes the following :

**1. Determination of the Water.**—As indicated in the
or more accurately by heating about 10 grams of the fat at
of hydrogen to constant weight.

**2. Determination of Extraneous Impurities** (soap
and gelatinous substances, etc.).—50 grams of the fat a
with a quantity of ether sufficient to dissolve the fatty ma

ccount is to be taken also of the fat combined as lime soap, treatment ubstance with ether is preceded by an hour's heating, with occasional g, on the water-bath with 3–5 drops of concentrated hydrochloric the lime soaps having been decomposed in this way, the further ure is as described above.

**Determination of the Ash.**—10 grams of the fat are carefully rated and the residue weighed. The ash of bone fat is composed of n oxide and a little carbonate, with small quantities of calcium phos- alumina and ferric oxide.

**Titer.**—As with tallow, the titer of bone fat is given by the solidifying f the free fatty acids, this being determined as in the case of tallow

**Acid and Saponification Numbers.**—By the general methods, 8. The acidity is expressed as percentage of oleic acid.

**Hydroxy-acids.**—As in General Methods, 15.

**Unsaponifiable Substances.**—These may be estimated by saponi- the fat with alcoholic potash and extracting the aqueous solution of ap with ether (*see* General Methods, 19).

**Recognition of Bone Fat which has been extracted with Ben-** —According to Gianoli,[1] this may be effected as follows:

) The fat is subjected to prolonged distillation with concentrated m chloride solution; where the fat has been extracted with benzine, rops which are not soluble in soda float on the surface of the distillate.

) The fat is saponified with alcoholic sodium hydroxide, the alcohol ed, the fatty acids liberated and washed with water, and this water d in the hot with ammonia: turbidity indicates the use of benzine.

**Test for American Bone Fat.**[2]—To ascertain if a sample of bone American origin may be used without inconvenience for soap-making, ollowing test is recommended:

0 grams of the fat and 30 c.c. of water are well shaken in a steam-heated vessel with 20 grams of sulphuric acid (66° Baumé), ass being afterwards heated and then left to stand: if the fat separates ly and rapidly, it may be regarded as of good quality, but if an emulsion ult to separate forms, the fat will give poor results and a bad yield of rine.

***

*mmercial bone fats* may have somewhat varying characters and com- on: the water content usually ranges from 1 to 3%, but may reach even extraneous impurities vary from 0·5 to 3% and the ash also from 0·5 . The titer for good products is 36–44°, the acidity may exceed 50%, saponifiable matters usually lie betwe n 0·5 an 3%.

## FOOT OIL

This is obtained more especially from the feet of the o those of the sheep and horse. It is a pale yellow, almost solidifying only below 0° (at about $-5°$). Its characters Table XLVII.

**Detection of Adulterations.**—The oil may be adulterat vegetable or marine animal oils, these additions being dete mining the various characters of the oil. Mineral oils lo gravity and the saponification and iodine numbers and m by investigation of the unsaponifiable substances (*see* Gener Vegetable oils give Bellier's reaction and the other gene seed oils (*see* General Methods, 23). By means of the spec tests, colza, cottonseed and sesamé oils (*q.v.*) may be foot oil gives no colour reaction and does not contain arachic acids or erucic acid. The presence of phytosterol would adulteration with vegetable seed oil (*see* Hog's Fat). Ma raise the specific gravity and the iodine number and may the special reactions indicated in the article on fish oils,

⁂

For use as lubricants, foot oil should remain liquid and long time, should not contain more than 2% of free acids c acid, and should not contain extraneous oils. A drop lying a glass plate and kept at 50° for 24 hours should not resini should be easily removable from the glass.

## Fish and other Marine Animal C

These oils may be divided into three classes: (1) *F* obtained from herrings, sardines, pilchards, sprats, tunn from the residues obtained in the preparation of these fi *oils* (*train oils*), from the marine mammifers, the seal and *Liver oils*, mainly from cod-liver but to a small extent fron ray, skate, etc.

Fish and blubber oils and cod-liver oil are treated sepa following articles; here, however, we shall give certain which are common to the three classes of oil and serve to dis oils from other fatty substances, either animal or vegeta

| … Fat. | Specific Gravity. |  | Melting Point °C. | Solidifying Point °C. | Zeiss butyro-refractometer Reading. |  | Maumené Number (J = Jean, T = Tortelli apparatus). | Saponification Number. | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fat… |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | t. |  |  |  | t°. |  |  |  |  |  |  | Melting Point °C. | Sol difyi… Point °C. |
| . . | 15 | 0·913 | — | 9 | — | — | — | 203–204 | 80–81 | — | — | — | — |
| . . . | 15 | 0·914–0·916 | 20–30 | 15–25 | — | — | — | 170–195<br>(185–190) | 44–75<br>(50 | 86–94 | — | 30–45 | 28–42 |
| . . | — | — | — | 34–35 | — | — | — | — | 36–39 | — | — | — | — |
| tic) . | — | — | 36–39 | 22–24 | — | — | — | — | 58–59 | — | — | — | — |
| . . . | 15 | 0·914–0·915 | 22 | 8–10 | 25 | 68–69 | 47–49 J | 184–192 | 64–82 | 95 | 0·4–0·7 | 34–39 | 30–35 |
|  | 100 | 0·881 |  |  |  |  |  |  |  |  |  |  |  |
| . . . . | 15 | 0·924 | 33–40 | 21–27 | — | — | — | 193–194 | 66–67 | — | 2 | 38–40 | 32–34 |
| mestic) | 15 | 0·922–0·930 | 25–34 | 18–22 | — | — | — | 191–198 | 58–71 | 92–96 | 1–2 | 37–41 | 31–38 |
| *rd*) . . | 15 | 0·931–0·938 | 36–48 | 26–32 | — | — | 39–40 T | 195–200<br>(196) | 46–70<br>(60–66) | 95–96 | — | 35–47 | 34–40 |
|  | 100 | 0·861–0·862 |  |  |  |  |  |  |  |  |  |  |  |
| . . . | 15 | 0·918–0·933 | 25–39 | 20–30 | — | — | 53–54 T | 195–200 | 78–95 | 94–97 | 0·4–2 | 36–42 | 30–38 |
|  | 100 | 0·861 |  |  |  |  |  |  |  |  |  |  |  |
| il . . | 15 | 0·913–0·927 | — | below 0 | — | — | 58–59 T | 195–197 | 73–90 | — | — | 30–32 | 28–29 |
| . . . | 15 | 0·913–0·920 | — | —5 | 40 | 52 | 45–47 T | 191–196 | 69–83<br>(70–75) | 97–98 | — | 35 | 31 |
|  | 100 | 0·826 |  |  |  |  |  |  |  |  |  |  |  |
| . . . | 15 | 0·962 | 49–52 | 37–38 | — | — | — | 195 | 35 | — | 1–2 | 53–55 | 48–50 |
| oil (ox | 15 | 0·914–0·919 | — | below 0 | 20 | 64 | 40–41 T | 189–200 | 64–78 | 95–96 | ·1–2 | 28–35 | 26–27 |
| . . . . | 100 | 0·862 |  |  |  |  |  |  |  |  |  |  |  |
| fat . . | 15 | 0·931–0·938 | 37–45 | 29–38 | — | — | — | 195–199 | 39–55 | — | 2 | 44–46 | 39–40 |
| . . . . | 15 | 0·943–0·953 | 40–49 | 27–37 | 40 | 44–49 | 31–42 T | 193–202 | 36–56<br>(40) | 95–96 | 0·5 | 43–48 | 38–47<br>(42–45) |
|  | 100 | 0·860–0·863 |  |  |  |  |  |  |  |  |  |  |  |
| oil . . | 15 | 0·917–0·918 | — | below 0 | — | — | 41–52 T | 194–197 | 68–75 | 95 | 0·7 | 24–26 | 21–22 |
| ow . . | 15 | 0·937–0·961 | 44–52 | 32–41 | — | — | — | 192–197 | 32–46 | 95–96 | — | 45–55 | 40–48 |
|  | 100 | 0·858–0·860 |  |  |  |  |  |  |  |  |  |  |  |
| rysalis fat | 25 | 0·920–0·927 | — | 0–3 | 20 | 76 | — | 190–194 | 113–146 | — | 0·6 | 34–37 | 28–35 |
|  | 40 | 0·910 |  |  |  |  |  |  |  |  |  |  |  |
| . . . . | 15 | 0·916 | — | — | — | — | — | — | 55–57 | — | — | 34–39 | — |
|  | 100 | 0·794 |  |  |  |  |  |  |  |  |  |  |  |

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[1] Numbers in brackets indicate the more common limits and mean values.

liquid is filtered through a steam-heated filter and the pre in benzene washed with boiling benzene, dried, and a det of its melting point, which should be above 190° (with position and blackening). If the melting point is below 190 is taken up several times with boiling benzene until a porti this temperature is obtained.

A reaction similar to the above is given also by the dr walnut and hempseed oils (*see* Linseed Oil) ; the hexabrom nished by these oils are, however, soluble in boiling benzene 180° without decomposing.

According to Marcusson, the octabromo-compound test made on the fatty acids and not on the oil as such—is able marine animal oil mixed with linseed or other oil.

(*b*) TORTELLI AND JAFFE'S REACTION. In a graduate with a ground stopper, 1 c.c. of the oil, 6 c.c. of chlorofo glacial acetic acid are shaken together and 40 drops of a bromine in chloroform added ; the cylinder is again shak a moment and then placed on a white paper and the col observed. Marine animal oils in general give a green c yellowish or blue reflexion, which increases during the spac and afterwards changes to brown. With vegetable or t oils and fats, pale yellow or yellowish colorations are obta ually darkening for an hour and then changing to brow

For the reaction to succeed, the oil and the reagents n dehydrated and the vessels very dry. If the oil is highly be decolorised with sulphuric acid[1] or soda.[2]

## FISH AND BLUBBER OILS

*Fish oils* proper are those obtained from the residues preparation of various fish (sardines, herrings, shad, tunnyf cetaceans are obtained mainly *Whale oil* and *Seal oil*, dol poise oil being less common. In general these oils are they are turbid and contain more or less abundant solid

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[1] 50 c.c. of the oil are treated for 5–6 hours, with occasiona gram of conc. sulphuric acid and then filtered through a thin lay the filtrate is washed with boiling water to render it free from acid paper in an oven at 100°.

[2] 100 c.c. of the oil and 5 c.c. of 30% caustic soda solution are h bath for a quarter of an hour with frequent shaking, 50–60 c.c. o chloride solution being then added and the heating on the water- three-quarters of an hour with shaking. The oil is then decante

With alcoholic potash they mostly give brown soaps; they contain quantities of unsaponifiable substances (0·5–2%). When dissolved bon disulphide and treated with a little conc. sulphuric acid, they reddish-brown coloration with no trace of violet (*see* Cod-liver Oil). give the general reactions for marine animal oils described above heir characters are given later in Table XLVIII.

eir analysis includes the following:

**Water, Impurities, Acidity.**—These are determined as in General ods, 1 and 7.

**Distinction between Fish Oils and Blubber Oils.**—With pure one kind or the other, the iodine and Maumené numbers are sufficient ermine if it is fish oil or whale (or seal) oil (*see* Table XLVIII). Mix- of the two types of oil cannot be identified.

e reaction with carbon disulphide and sulphuric acid serves to dis- sh fish and blubber oils from liver-oils (*see* following article).

**Detection of Impurities:**

) MINERAL AND RESIN OILS. These are detected by saponifying the 0–100 c.c.) and extracting and examining the unsaponifiable matter dicated in General Methods, 19.

) VEGETABLE OILS. These are detected by the digitonin test for osterol (*see* Hog's Fat). Cottonseed and sesamé oil may also be iden- by means of their special colour reactions, provided that the oil is not nuch coloured.

## COD-LIVER OIL

his is obtained from the liver of *Gadus morrhua* and of other allied fish e Northern Atlantic. According to its purity and colour it is divided *white* (medicinal, superior), which is clear, of pale or straw yellow r, almost odourless and almost tasteless; *pale*, which is clear, reddish- w, and with a marked fishy odour and taste; *red* or *brown*, which is more ss turbid and brownish-red and with an unpleasant fishy odour and .

t dissolves slightly in alcohol, but easily in ether, benzene or other ary fat solvent. It contains small quantities of unsaponifiable sub- ces (mainly cholesterol): 0·3–2% in pale oils and up to about 8% in e brown ones.

Further it contains traces of iodine in organic combination (0·0002– %). This is not extractable by solvents or by mere saponification, but etected only by saponifying the oil, adding a little nitre to the soap,

TABLE XLVIII

## Characters of Marine Animal Oils[1]

| | Specific Gravity. | Setting Point. | Zeiss Butyro-refractometer Reading. | Maumené Number (J = Jean, T = Tortelli apparatus). | Saponification Number | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty Acids. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Melting Point. | Setting Point. | Acetyl Number. |
| ISH OILS | | | | | | | | | | | |
| *losa menhaden Cuv.*) | 0·927–0·933 15°) | — | 71–72 (40°) | 123–128 J | 188–193 | 160–179 | — | 2–3 | — | — | — |
| *pea Harengus*) . . | 0·920–0·939 (15°) | — | — | — | 170–194 | 103–142 | 95–96 | — | 30–32 | — | — |
| rdine (*Clupanodon*<br>T. S.) | 0·928–0·935 (15°) | — | — | — | 189–196 | 160–190 | 95–97 | — | 35–36 | — | — |
| ne . . . . . . | 0·875–0·878 (100°) | — | — | — | 193–200 | 154–159 | — | — | — | — | — |
| rdine (*Clupea sar-* | 0·928–0·934 (15°) | 20–22° | — | 112–113 T | 189–196 | 160–193 | 94–96 | — | 30–31 | — | 21–22 |
| *sprottus*) . . . | 0·927–0·928 (15°) | — | 76 (25°) | — | 194–195 | 122–142 | 95 | 1–2 | 28 | 25–26 | 8–9 |
| *mnus vulgare, T.* | 0·932–0·933 (15°) | — | 89 (20°) | — | 185–186 | 156–199 | 95–96 | — | 31 | — | 22–29 |
| VER-OIL OF<br>*norrhua*) . . . . | 0·920–0·938 (15°) | below 0° | 75–85 (25°) | 102 T | 171–193 (185–190) | 135–182 (150–170) | 95–97 | 0·2 | 21–25 | 13–24 | 19–51 |
| *alus spec.*) . . . | 0·910–0·929 (0·915–0·917) (15°) | — | — | 90 J | 146–183 (160) | 90–138 | 97–98 | 1–2 | — | — | 66 |
| *tis, R. Clavata*). . | 0·931 (15°) | — | — | — | 185–186 | 157 | 94–95 | 1 | — | — | 10–11 |
| BBER OILS | | | | | | | | | | | |
| *ena mysticetus, B.* | 0·916–0·930 (15°)<br>0·872 (100°) | — | 65 (25°) | 75–76 T | 160–202 (180–190) | 90–146 | 93–95 | 1–4 | 14–27 | 10–24 | 11–23 |
| n the body (*Delphi-* | 0·918–0·930 | — | 65–69 | — | 197–231 | 99–127 | 93 | 11–44 | — | — | — |

**Acid Number.**—As in General Methods, 7.

**Test for Added Iodine (Inorganic).**—About 10 c.c. of oil are en with as much water, the latter being then separated and treated starch paste and either conc. nitric acid or chlorine water: appear- of a blue coloration indicates inorganic iodine.

. **Freezing Point.**—The oil is maintained at 0° for some time to tain if it remains liquid.

. **Detection of Adulterations.**—The oil may contain the following xtures:

) OTHER FISH-LIVER OILS. No certain methods are known of dis- ishing different fish-liver oils or their mixtures.

) FISH AND BLUBBER OILS. No certain method exists of detecting il in cod-liver oil. Addition of blubber oil (whale, seal) may be sus- d as a result of determinations of the iodine number, the Maumené oer and the refractometer reading (Zeiss), which are lowered by whale al oil (*see* Table XLVIII).

) VEGETABLE AND MINERAL OILS. These are recognised by the ods given in the preceding article (Fish and Blubber Oils).

⁂

ccording to the Official Italian Pharmacopœia, *medicinal* cod-liver oil is r or straw-yellow, D at 15° = 0·922–0·930, iodine number = 150–17 . cooled to 0° it does not congeal, but deposits flocks of white solid matter. ould give the reaction for fish-liver oils and should contain no inorganic e (test 3).

e acidity is low in white oils, especially in so-called steam liver oil (0·3– s oleic acid), but is higher (up to 8%) in the more highly coloured yellow le oil and may reach about 30% in brown oils.

## Waxes

Vaxes are composed essentially of compounds of certain fatty acids itic, stearic, cerotic) with higher alcohols (cetyl, myricyl alcohols); contain also a certain amount of free acids (beeswax, carnauba wax) solid hydrocarbons (beeswax). Waxes are of animal origin, such as vax, Chinese insect wax, wool fat and spermaceti, and of vegetable , such as carnauba wax, fig wax, ocuba wax, etc. The latter should oe confused with other vegetable products known as waxes, these being y fats, such as Japan wax and myrtle wax (*see* Vegetable Fats).

importance are: beeswax, wool fat, spermaceti

*Crude* (*virgin*) wax in pale yellow or brown. Europea
yellow or pale yellow, the African and American reddish-y
and the Indian greyish-brown. It is fatty to the touch and
to the heat of the hand, and presents a granular fracture.
odour, recalling that of honey, and a faintly balsamic tas

*White or bleached* wax (decolorised by air and light or by c
is white, brittle, and only slightly fatty and odoriferous.

In general the wax is almost insoluble in cold alcohol bu
in boiling absolute alcohol, from which it separates on coolin
soluble in cold ether, more so in boiling ether, chlorofor

It consists principally of cerotic acid and myricyl palm
but contains also free melissic acid and ceryl alcohol an
(3–12%, according to the origin).

The physical and chemical characters of different types
given in Table XLIX.

The wax may be adulterated with stearine, colophon
or ceresine, Chinese (insect) wax, carnauba wax, Japan
tallow, wool fat, flour or starch, and mineral substances ;
be present. The colour may be enhanced by turmeric or

Imitations of the wax are made with paraffin wax, ceresin
or with various mixtures of paraffin wax, carnauba wax, Japa
etc., often coloured with coal-tar colours.

To detect the different adulterations and imitations h
is necessary to determine the various characters (*see* 1–5)
apply certain special tests (*see* 6–13), since it is possible to
with the characters of the pure wax. If, on the other han
of beeswax in mixtures with other substances is required, tes

In the case of the crude (virgin) wax, before proceedin
(with the exception of the determinations 12), it is well to
with water to remove the whole of the honey and then t
mass in the hot.

**1. Specific Gravity.**—This may be determined most e
of the specific gravity bottle, but Hager's method may als
wax is melted at a gentle heat and poured in drops into c
the beads of wax thus obtained being dried in absorbent
night to solidify and then immersed in alcohol of known
e.g., 0·965, at 15°. If the beads remain suspended at a
liquid, the specific gravity of the wax is that of the liqui
on the other hand, they sink or float, tests are made wit
more concentrated alcohols until the correct s ecific gra

ked name, the wax being difficultly saponifiable.

re exact determinations may be made by Berg's method, modified hrisch and Kurschner: about 4 grams of the wax, 20 c.c. of xylene ly distilled) and 20 c.c. of absolute alcohol (neutralised) are boiled flux apparatus for 5–10 minutes; titration of the liquid with semi- l alcoholic potash (with phenolphthalein) gives the acid number. her quantity of 30 c.c. of the same potash solution is then added, uid boiled for an hour, treated with 50–75 c.c. of 96% alcohol (neu- l), heated for 5 minutes longer, and the excess of potash titrated eminormal hydrochloric acid (indicator as above); the ester number s obtained.

udging a wax (*see* later) it is important to know the acid, saponification *er numbers*, the last being the difference between the first two. ratio of ester number to acid number, the so-called *ratio value*, is also ortance.

**Iodine Number.**—As in General Methods, 12.

**Refractometric Reading.**—This is determined with the Zeiss -refractometer (*see* Butter, Vol. II, Chapter II) at a temperature of To reduce the reading to the normal temperature of 40°, the difference n 64 and 40, i.e., 24, is multiplied by 0·53 and the product added to ding at 64°.

**Test for Stearine.**—About 3 grams of the wax and 10 c.c. of 85% are heated and shaken in a flask until the wax is thoroughly fused en left to cool for some hours with frequent shaking; only the stearine lso any resin, *see* later, 7) remains in solution. The solution is then and the filtrate diluted with a large amount of water. With the ax the liquid remains clear, whereas the presence of stearine (about more) produces a marked turbidity or a white precipitate, which e collected and identified by means of its melting point (53–55°) ponification number (about 195), provided of course that Morawski's n indicates that resin is absent.

n resin and other extraneous acid substances soluble in alcohol are the stearine (S) added to a wax may be calculated from the acid found ($a$) by means of the formula:

$$S = \frac{100(a - 20)}{175}.$$

en a wax or a mixture resembling wax contains stearic acid and t is well to eliminate these substances immediately by means of 85% and to make the other tests and determinations on the insoluble

20).

The quantitative determination may be effected by Tw (*see* General Methods, 20).

**8. Paraffin Wax and Ceresine.**—As a preliminary the wax, about 25 c.c. of seminormal alcoholic potassiu 20 c.c. of 95% alcohol are boiled for an hour in a reflux a naked flame: with pure wax the solution is clear, or almost cl so when diluted with hot water, but with wax mixed wi or ceresine, the liquid remains turbid, and becomes still more with water.[1]

A more certain and even *quantitative* test may be method[2]: 10 grams of the wax, 25 c.c. of alcoholic po KOH per litre of absolute alcohol) and 50 c.c. of pure be for 20 minutes in a reflux apparatus on an asbestos card ove 50 c.c. of water being then added and the boiling continue After a short rest, the liquid separates into two layers: yellowish one (benzene solution of higher alcohols and hy a lower, somewhat opalescent one (aqueous-alcoholic soa soon as the separation is sharp, the lower hot liquid is drawn by 50 c.c. of hot water, and the liquid boiled for 10 minut apparatus. The aqueous solution is then immediately the benzenic liquid transferred to a tared capsule, the va which the operations have been conducted being washe benzene[3]; the solvent is then evaporated on the water-batl dried at 100° and weighed. This gives the total weight of and hydrocarbons contained in the wax and from this the co ous hydrocarbons may be deduced, knowing that in pure alcohols and hydrocarbons never exceeds 55% (usually 50%).

If desired, the hydrocarbons may, according to Ley quantitatively from the higher alcohols by means of a alcohol and conc. hydrochloric acid, in which the latter diss paper); or, as Buchner recommends,[4] the acetyl numb Methods, 11) of the mixed higher alcohols and hydrocarbon mined and the quantity of the former deduced by taking acetyl number of the higher alcohols of the pure wax.

**9. Test for Carnauba Wax and Insect or Chin** special reactions exist for identifying these waxes in beeswa ever, the presence of other extraneous substances has bee any stearic acid and resin eliminated as indicated above (6 r (*see* later).

**Test for Japan Wax** (from various species of *Rhus*), **Tallow ther Fats in general.**—A scrap of fused potassium bisulphate is to about 1 gram of the molten wax in a test-tube and the mixture y heated over a direct flame: the pure wax gives pungent sulphurous whereas in presence of fats (glycerides) the characteristic irritating of acrolein (due to decomposition of the glycerine) is observed and of filter-paper, soaked in a solution of sodium nitroprusside and piperidine and placed at the mouth of the tube, turns violet-

his test shows the presence of glycerides, the glycerine is determined eneral Methods, 17: the amount of glycerine, multiplied by 10, gives imately the quantity of fatty substance in the wax, since fats contain average about 10% of glycerine.

should also be borne in mind that Japan wax, tallow and other fats he melting point and raise the saponification number (tallow raises e iodine number) of the wax (*see* later).

**Detection of Wool-Fat and its Products (Wool-Fat Stearine x).**—The higher alcohols and hydrocarbons are extracted from the y Leys' method (8), the mixture thus extracted being tested for erol by means of chloroform and sulphuric acid (*see* General Methods, gher Alcohols).

**Determination of the Water and Various Extraneous Im- s.**—About 5 grams of the wax as it stands are heated at 100–105° stant weight, the loss representing the water. The residue is dis- in hot benzene and the solution filtered from any appreciable undis- portion through a tared filter, the insoluble matter being washed ith hot benzene, dried at 100° and weighed.

e residue insoluble in benzene is then tested for starchy or mineral s by the usual methods.

. **Extraneous Colouring Matters.**—About a gram of the rasped s shaken with ammonia: in presence of *turmeric*, a reddish-brown tion is obtained.

detect *coal-tar dyes*, the wax is extracted with 90–95% alcohol in t. The liquid is then cooled well at 15° for some hours and filtered, trate being evaporated and tested for artificial colouring matters (*see* ar Dyes in Vol. II). As a rule imitation wax and wax substitutes loured with the so-called Soudan dyes, which are turned pink with hydrochloric acid.

. **Detection of Beeswax in Mixtures with other Substances.**—

of different kinds, such as paraffin

insect wax, which contains ceryl alcohol.

(*a*) By means of the Acetyl Number. The substanc
and the unsaponifiable part extracted by the usual method
by Leys' method (*see* 8) and its acetyl number determine
Methods, 11). If this number is found to be zero, the prese
may be excluded ; if, however, there is an acetyl number,
the wax may be assumed and the amount may be calculated
from the fact that the mean acetyl number of the higher
wax is 122 and that the wax contains, on the average, about
alcohols.

(*b*) By transformation of the Myricyl Alcohol
Acid. 5 grams of unsaponifiable substance, extracted
ceding test, are intimately mixed with about 10 grams of
lime and a little caustic soda, the mixture being placed in a
and this plunged into a sand-bath and heated to 200–22
the temperature is measured with a thermometer immersed i
and used at intervals as a stirrer. When cold, the substa
with petroleum ether, the solvent evaporated and the r
If the weight is equal or nearly equal to that of the subs
presence of wax is excluded, but if the petroleum ether extra
less in weight than the substance taken, wax may be p
latter case the difference between 5 grams (weight of subst
the weight of the residue represents the myricyl alcohol c
5 grams of unsaponifiable matters. If, then, the percenta
fiable matter in the substance is known, the myricyl alco
100 parts of the substance itself and hence approximately
of the wax present may be calculated, since 38 parts of
correspond on the average with 100 parts of beeswax.

⁂

The purity of a wax is judged first of all from the results o
tions of the various characters, account being naturally tak
and nature of the wax : if all or some of these characters lie o
indicated in Table XLIX, the wax is not genuine.

A low specific gravity indicates the presence of solid par
stearic acid or tallow, and a high one that of carnauba wax, Ja
phony.

The acid, saponification, ester, ratio, iodine and refract
are also influenced more or less by the presence of various fo
as is shown in the following table (page 439), where the me
ordinary virgin wax are compared with those of the substanc
employed to adulterate it.

It should, however, be noted that mixtures may be prepared

| | Gravity at 15° C. | Melting Point | Acid Number | Saponification Number | Ester Number | Ratio Value | Iodine Number | Refractometric Degree at 40° C. |
|---|---|---|---|---|---|---|---|---|
| | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* |
| ıx . . | 0·964 | 63° | 20 | 95 | 75 | 3·70 | 10 | 44 |
| wax . . | 0·970 | 82° | 0 | 63 | 63 | 63 | — | 46 |
| ba wax . | 0·995 | 85° | 4 | 79 | 75 | 18·75 | 10 | 66 |
| wax . . | 0·990 | 53° | 20 | 220 | 200 | 10 | 9 | 47 |
| e . . . | — | below 55° | 195 | 195 | 0 | 0 | — | — |
| . . . . | 0·948 | 42° | 4 | 195 | 191 | 48 | 40 | 47 |
| colophony) | 1·100 | above 70° | 180 | 190 | 10 | 0·06 | 115 | — |
| araffin . | 0·870 | below 65° | 0 | 0 | 0 | 0 | 0 | 22 |
| e . . . | 0·920 | above 60° | 0 | 0 | 0 | 0 | 0 | 40 |

## WOOL FAT

ıs is obtained from wool by washing with soap or alkali carbonate n or by extracting with a solvent (carbon disulphide or benzine). e crude fat is utilised especially for the preparation of lanoline and d wool fat, from which wool fat oleine and stearine are prepared. tter products are dealt with in the next chapter (Industrial Products he Treatment of Fatty Matters); here we shall deal only with crude urified wool fat and lanoline.

### *A.* Crude Wool Fat

s has a tallowy consistency, a yellow or brown colour, and a peculiar, ing odour. It is slightly soluble in alcohol, and more so in ether, orm, benzene, etc.; it saponifies with difficulty. Its physical and l characters are given later in Table XLIX, dealing with animal It is dextro-rotatory ($[\alpha]_D^{35^\circ}$ = about 6–9° in chloroform solution), acid number may vary from about 10 to 50 (5–25% of free acids ted as oleic acid) according to the method used in its extraction. cination it leaves little ash (1–5%).

contains marked quantities of unsaponifiable substances (40–50%), ng mainly of cholesterol and isocholesterol, and consequently gives ction of these higher alcohols with chloroform and sulphuric acid neral Methods, 19, 1, Higher Alcohols). It may also contain water rious foreign impurities in varying quantities.

de wool fat is readily identified by its external characters and by esterol reaction. In analysing it, it is usually sufficient to determine

is carefully poured on to 5 c.c. of conc. sulphuric acid, at the zo
of the two liquids there is produced a bright brownish-red colo
reaches its maximal intensity after 24 hours.

The most important tests to be made on *lanoline*, especi
pharmaceutical purposes, are :

**1. Water and Ash.**—10 grams are heated at 100–110°
weight, the residue being carefully incinerated and the ash

**2. Acidity.**—As in General Methods, 7.

According to the Official Italian Pharmacopœia, the test
made by dissolving 2 grams of the lanoline in 20 c.c. of petr
adding 2 drops of phenolphthalein solution and then 0·5 c.c.
sodium hydroxide solution : the liquid should be coloured a p

**3. Other Tests.**—The lanoline is heated with aqueous
solution to ascertain if ammonia is evolved. 10 grams of
heated on the water-bath with 50 grams of water : a clear
coloured layer of fused fat should form at the surface of the
impure lanoline a brown, turbid and frothy mass is obtaine

⁂

Pure anhydrous lanoline should contain only traces of moist
emulsified with water should contain not more than 30 % of the lat
it should have little ash (at most 0·05%), give no acid reactio
paper, correspond with the Official Italian Pharmacopœia test
no ammonia when heated with soda solution.

## Spermaceti

This is the solid portion obtained by cooling and pressu
oil contained in the cephalic cavity of the sperm whale or cach
*macrocephalus*) and allied species.

Refined or pure spermaceti of commerce is in white, har
masses (thin sheets), slightly fatty to the touch and almost
the air it becomes yellowish and rancid.

It dissolves in boiling alcohol, from which it crystallises on
it is soluble also in ether, chloroform, benzene and carbon di
dissolves very slightly in cold 98% alcohol and is insoluble in
or in water. Its physical and chemical characters are given in

Spermaceti consists mostly of *cetin* (the cetyl ester of pa
m.pt. 53·5°, and contains 50–52% of unsaponifiable substan

**Detection of Adulterants.**—Additions of ceresine or s
stearic acid (stearine), tallow and beeswax are made, but only
extraneous substances easily destroy the characteristic crystalli

| Nature of Wax. | t° | Specific Gravity. | Point °C. | Point. °C. | t° | Refractometer Reading. | Number A | cation Number. | Number E | E A |
|---|---|---|---|---|---|---|---|---|---|---|
| ANIMAL WAXES | | | | | | | | | | |
| ary beeswax.<br>*ifera*) | 15 | 0·941–0·976<br>(0·964) | 60·5–66·5<br>(63) | 60–61 | 40 | 43·2–45·7<br>(44) | 16·7–23·6<br>(20) | 88–106<br>(95) | 65·9–85·0<br>(75) | 2·8–4·5<br>(3·7) |
| hed in the sun | 15 | 0·964–0·973<br>(0·966) | 63–64 | 61–62 | 40 | 44 | 19–23<br>(20) | 90–98<br>(95) | 71–76<br>(75) | 3·7 |
| | 100 | 0·818–0·827 | | | | | | | | |
| hed chemically | — | — | 63–64 | 61–62 | — | — | 16·8–24 | 93–108 | 71–84 | 3–4 |
| sed | — | — | — | — | — | — | 21–22 | 81 | 59–60 | 3 |
| acted (with solvents) | 15 | 0·949–0·984 | 59–72 | — | — | — | 15–28 | 64–102 | 49–78 | 2·4–3·4 |
| wax (Ghedda wax), crude<br>*sata*, *A. florea*, *A. indica*) | 15 | 0·966 | 60–69<br>(63–64) | — | 40 | 44–46 | 5–13<br>(7–8) | 75–145<br>(100) | 70–124<br>(93) | 7–18<br>(13) |
| (Chinese wax)<br>*riferus*, Fabr.) | 15 | 0·926–0·970<br>(0·970) | 81–83 | 80–81 | 40 | 46 | 0 | 63–93<br>(63) | 63–93<br>(63) | 63 |
| | 100 | 0·810 | | | | | | | | |
| ude | 15 | 0·973 | 39–42 | — | — | — | 10–50 | 77–146 | — | — |
| ied (Anhydrous lanoline) | 15 | 0·978 | 36–42 | 38–40 | — | — | 0–1 | 98–127<br>(100) | — | — |
| | 100 | 0·901–0·902 | | | | | | | | |
| | 15 | 0·940–0·960 | 44–55 | 43–48 | — | — | 0–5 | 108–135 | — | — |
| | 100 | 0·808–0·842 | | | | | | | | |
| oil | 15 | 0·875–0·890 | — | — | 25 | 54 | — | 117–150<br>(132) | — | — |
| | 100 | 0·833 | | | | | | | | |
| oil (Arctic sperm oil).<br>*don rostratus*) | 15 | 0·876–0·905 | — | — | — | — | — | 121–136 | — | — |
| | 100 | 0·827 | | | | | | | | |
| VEGETABLE WAXES | | | | | | | | | | |
| wax<br>*ia antisyphilitica*) | 15 | 0·950–0·993 | 67–92 | 64–75 | — | — | 10–21 | 47–65 | 34–53 | — |
| vax<br>*cerifera* L.) | 15 | 0·990–1·000<br>(0·995) | 83–86<br>(85) | 80 | 40 | 65–69 | 4–8<br>(4–5) | 79–95<br>(79–80) | 75–80<br>(75–76) | 18–19 |
| | 100 | 0·842 | | | | | | | | |
| (from the fruit of *Myristica* | | | | | | | | | | |
| | 15 | 0·920 | 40 | — | — | — | — | — | — | — |
| (*Ceroxylon andicola*) | 15 | 0·992–0·995 | 102–105 | — | — | — | — | — | — | — |
| x (*Musa spec.*) | 15 | 0·965–0·970 | 79–81 | — | — | — | 2–3 | 109 | — | — |
| x (*Raphia Ruffia*) | 15 | 0·950 | 80–82 | — | — | — | — | — | — | — |
| ax | — | — | 60 | — | — | — | — | — | — | — |

[1] The numbers in brackets indicate the more common limits and mean values.

Methods, 4, 7, 8 and 19). Addition of stearine or wax gives
while that of tallow or other fat increases the saponification
paraffin or ceresine lowers the saponification number an
amount of unsaponifiable matter.

The two following tests are prescribed by the Official
copœia:

1. Solubility in Benzene. 1 gram of the spermace
in 3 grams of benzene at a gentle heat: on cooling the liqui
clear.

2. Test for Stearic Acid. 1 gram is boiled with
alcohol and 1 gram of dry sodium carbonate, and filtere
when acidified with a dilute acid, should become barely
precipitate indicating the presence of stearic acid.

⁂

According to the Official Italian Pharmacopœia, pure sp
have no odour of fish, should have a specific gravity 0·940–0
melt at 50–54° or, if recrystallised from alcohol, at 54–55°; th
tion should not have an acid reaction; tests 1 and 2 should

## SPERMACETI OIL

This is the liquid part of the oil contained in the cephal
cachalot and allied species.

The ordinary refined spermaceti oil of commerce is an a
or pale yellow liquid, mobile and nearly odourless.

It is a liquid wax, consisting mostly of esters of one
alcohols with fatty acids of the oleic acid series (fisetoleic
tains 37–45% of higher alcohols (unsaponifiable substances)
of fatty acids combined with these alcohols; it contains
quantities (0·1–0·4%) of free acids and it turns rancid with
Its characters are shown in Table XLIX.

**Detection of Adulterations.**—Adulteration with mine
oils is common. These may be detected by determining the s
saponification and iodine numbers, and unsaponifiable subs
in mind the following:

1. Mineral Oils. These lower the saponification numb
the content in unsaponifiable substances. If the latter
acetic anhydride and then cooled, the mineral oils separa
pletely from the liquid (*see* General Methods, 19).

2. Fatty Oils. These raise the specific gravity and th
number and diminish the proportion of unsaponifiable sub

## CHAPTER X

# INDUSTRIAL PRODUCTS

## ROM THE TREATMENT OF FATTY MATTERS

most important industrial products obtained from the treatment matters are: boiled linseed oil, oxidised oils, hardened or hydro- oils, Turkey-red oils, oleine, stearine, candles, soap and glycerine. methods of analysis used for these materials are largely those em- with fatty substances, being based mainly on the determinations various characters (specific gravity, melting point, acid number, cation number, iodine number, etc.), for which the general methods eceding chapter are used. Any special tests necessary are described, sion offers, in the following articles.

## BOILED LINSEED OIL

ed linseed oil is fluid but more viscous than the crude oil, and is less brownish-yellow or brown and of a peculiar odour; there is ery thick, almost pasty form, which is brown with a greenish fluores- nd has a very marked odour.

eneral, the boiled oil is distinguished from the ordinary or crude the appearance, the smell, the high specific gravity (0·937–0·99), sence of drying agents (these are sometimes absent, in which case inction is readily made by other characters) and especially by the th which it dries.

ed linseed oil may be found mixed or adulterated with resin, resin eral oil, fish or blubber oil, or vegetable oil (colza, soja bean, etc.). lysis includes the following determinations and tests:

**pecific Gravity, Iodine Number, Saponification Number, umber.**—By the general methods given in the preceding chapter.

Oils boiled with resinates naturally contain small qua due to the dryer. Addition of resin should be assumed o alcoholic extract is large in amount and the acid number of (at least above 12; *see* later).

**5. Detection of Siccatives.**—This may be made on the or by dissolving the oil in ether and shaking with dilute n nitric acid solution being tested by the ordinary methods f ganese, calcium, zinc and cobalt.

**6. Drying Properties.**—A drop of the oil is spread u glass plate (5 × 10 cm.) and left in the air, protected from d at 15–20°. From time to time the course of the drying is test the oily layer hard with the finger: drying is complete w no longer adheres to the surface. The latter is then heated if cracking occurs.

Further, 25 parts of the oil are mixed intimately with 20 white or minium, the paste thus obtained being spread un iron plate and left to dry as before.

⁂

Good boiled linseed oil should satisfy the following require

That boiled at a moderate temperature should be only sli and should yield a perfectly white paste when mixed with pu white.

Its specific gravity should not be below 0·935 and as a ru 0·935 and 0·948, but oil heated at a very high temperature burned) may have a value as high as 0·99. The presence of (vegetable, animal, mineral) lowers the specific gravity.

The *iodine number* may vary from 150 to 172 in light boile fall to 70°, with those strongly boiled and dense.

The *saponification number* should lie between 190 and 195, by colza oil and especially by mineral or resin oil.

The *acid number* should not exceed 12 (usually it stands bet and is raised by free resin.

It should not contain *foreign oils* or free *resin*.

The content of *unsaponifiable substances* should not exceed 2

The amount of *dryer* should be such that the oil does not le 1% of ash.

In the *drying test*, pale oils should dry completely within 20 ones within 12 hours. After being heated at 100°, the dry la exhibit cracking and should become detached in scales when knife. When mixed with zinc white or minium, it should dry co 24 hours.

e are obtained by passing a current of air through a fatty oil at a ture of about 70–120° until the oil becomes thick and viscous like il. Colza, cottonseed, maize, foot and fish oils are usually employed purpose.

eneral, blown oils are dense, viscous, reddish-brown liquids with a odour (of boiled oil). In comparison with the corresponding original ey have high specific gravities, refractivities and saponification s and low iodine numbers (*see* Table, p. 446). Further, they contain quantities of hydroxy-acids, and it is characteristic of them that rnish deep brown fatty acids (almost black with blown fish oils), rtially soluble in ether.

lysis of these products is concerned principally with the two following

**Origin of the Blown Oil.**—It is somewhat difficult to state the of the original oil from which a blown oil is prepared, since the specific reactions no longer hold. An approximate orientation may be d by means of the following criteria.

fatty acids of oxidised *colza* oil are liquid and their lead salts are soluble in ether.

fatty acids of oxidised *cottonseed* oil are solid and their lead salts y soluble in ether.

fatty acids of oxidised *fish* oils are blackish and saponification of ils yields a black, pitchy substance insoluble in potash, alcohol or nd similar to the linoxyn of linseed oil. This does not occur with vegetable or foot oils. Blown fish oils are the ones showing the density accompanied by the highest iodine number.

lised *foot* oils exhibit a specific gravity equal to that of oxidised ole oils but a less iodine number.

**Mixtures of Blown Oils with Mineral Oils.**—Mixtures of heavy oil and oxidised oil (about 5–30%) form good lubricants for marine .

products are recognisable by the smell and by the following test: ns of the oil are saponified with 25 c.c. of alcoholic potash in the ay, heating for half an hour on the water-bath in a reflux apparatus requent shaking. Without evaporating the alcohol, the whole is rred to a separating funnel, diluted with 150 c.c. of water, shaken nd carefully and left to stand until sharp separation into two layers ace, the lower aqueous layer being then run off and the supernatant oil collected separately (with the help of a little ether), dried and

| | | Specific gravity at 15°. | Zeiss butyro-refractometer Number at 15°. | Saponification Number. | I N |
|---|---|---|---|---|---|
| Colza oil | ordinary . | 0·912–0·917 | 68–69 | 170–181 | 9 |
| | blown . . | 0·967–0·977 | 80 | 197–268 | 4 |
| Cottonseed oil | ordinary . | 0·922–0·925 | 68 | 191–198 | 10 |
| | blown . . | 0·972–0·979 | 80–81 | 213–226 | 5 |
| Ox-foot oil | ordinary . | 0·921 | 62 | 194 | |
| | blown . . | 0·972 | 73–74 | 241–242 | |
| Fish oil | ordinary . | 0·925 | 78 | 190–191 | |
| | blown . . | 0·980–0·985 | 90–91 | 247–248 | 7 |

## HARDENED OR HYDROGENISED O

These are obtained by subjecting liquid fatty oils, eith
animal, to the action of hydrogen at a temperature of 130-1
of a catalytic substance, usually finely divided reduced nicke
platinum and various metallic oxides. The unsaturated liq
(oleic, linoleic, etc.) of the glycerides of the oils are transfo
stearic acid, so that the oils themselves become solid.

These products, marketed under the names of *Talgol*, *Can*
are usually obtained by hydrogenising marine animal oils
whale oil), but they may also be prepared from vegetable o
soja-bean, castor, etc.).

As a rule, hardened fats are solid and of the consistency
very prolonged hydrogenation they acquire the hardness
they have persistent colours, odours and tastes which are s
of tallow but no longer recall the original oils. They usually
but the strongly hydrogenised ones have still higher melting
fatty acids melt at temperatures 2-3° below the points o
neutral fats. Their acid number is small and their saponi
normal (190-195), while the iodine number depends on the d
genation and may fall to a few units.

Hydrogenised oils give the general colour reactions of t
very similarly to the latter: thus, they give Hauchecorne's
and Bellier's reactions if they are derived from vegetable c

, as a rule, traces of the (mostly nickel) are found.

nalysis of these products includes :

**aracters and Origin.**—Of the characters of hardened oils, those l importance, besides the objective ones, are the melting point, g point of the fatty acids (titer) and the acid, saponification and mbers.

certain the origin of a hardened oil, the unsaponifiable substances must be extracted and identified (*see* Hog's Fat) : hardened animal in cholesterol and the vegetable ones, phytosterol.

Tortelli and Jaffe reaction (*see* p. 430) indicates if a hardened oil ed from a marine animal oil.

**st for Traces of Catalyst** (*Nickel*).—This may be made on the product or, according to Fortini, in the following way :

to grams of the fat are heated for half an hour on the water- as much conc. hydrochloric acid, with frequent, vigorous shaking ; is then filtered through a moist filter into a dish, evaporated to nd the residue moistened with a few drops of 1% alcoholic dimethy- solution : in presence of nickel a red coloration is obtained, this dered more evident when the solution is made slightly alkaline op of dilute ammonia.

extract of the acid is highly coloured it is well to redissolve it in ater and decolorise with animal charcoal.

## TURKEY-RED OIL

s obtained by treating castor oil with sulphuric acid, eliminating s of acid by washing with water and sodium sulphate solution and ralising more or less completely with ammonia or soda. It con- efore, essentially of *ammonium* or *sodium sulphoricinate*. It is ellow liquid with the odour of castor oil. It dissolves in a small of water but further addition of water (10 vols. per 1 vol. of the s a perfect, white emulsion which persists for some hours and is id to litmus paper. Sulphoricinates neutralised with ammonia ssolve, however, in water in all proportions, but faint acidification ution with a few drops of acetic acid results in emulsification. If of acid or sodium chloride is added, either to the emulsion or lution of a sulphoricinate, an oily layer separates.

oricinates are also completely dissolved by ammonia, the solution rendered turbid by dilution with water. Alcohol, too, completely them.

cinate or sulpholeate.

Analysis of Turkey-red oil comprises the following deter tests, the second and fifth being of special importance for of the product.

**1. Solubility and Emulsivity.**—2 or 3 c.c. of tl much water should give complete solution and addition of of water should then yield a persistent homogeneous emulsi acid reaction.

Dilute ammonia should also dissolve the oil completely a should remain clear on dilution with a large quantity of

**2. Total Fat.**—10 grams of the oil are heated somewh flask with 50 c.c. of water, 25 c.c. of dilute hydrochloric ac added and the liquid boiled for 3-5 minutes (until the fuse clear), allowed to cool, transferred to a separating funnel, flask is washed with a little water and with 200 c.c. of eth is vigorously shaken and allowed to stand, the acid aqueo removed and the ethereal solution washed with three succes of 15 c.c. of water, these wash waters being added to the aque and this kept for the determination of the sulphuric acid The bulk of the ether is distilled from the ethereal solutio flask and the residue transferred to a tared beaker; when of the ether has evaporated, the residual mass is dried for 1– a naked flame (a medium flame being passed under the b fat ceases to froth) and then for half an hour in an oven at 105 The weight of fat thus found, multiplied by 10, gives the total fat in the oil.

The fat may then be used for investigating the nature of (below).

**3. Determination of the Sulphuric Acid.**—The a obtained as above is precipitated with barium chloride, the w sulphate thus precipitated corresponding with the *total sulph* in the oil.

On the other hand the *sulphuric acid as ammonium or s* is determined by treating 10 grams of the oil with saturated s solution (quite free from sulphate), filtering through a moist well with the saturated sodium chloride solution, diluting t precipitating the sulphate in it with barium chloride.

Subtraction of the percentage of $SO_3$ as ammonium or so from the total percentage gives the *sulphuric acid* (as $SO_3$) as and this, multiplied by 4·725, gives the percentage of *sulph* in the oil.

an acetyl number below 140 show immediately
oil has not been obtained from pure castor oil. The specific colour
of the different oils (cottonseed, sesamé, etc.) may then be tried.
also to be borne in mind that the emulsive oils prepared with olive,
ed, colza, sesamé and similar oils do not usually give clear solutions
ohol, as does pure emulsive castor oil.

letecting mineral or resin oils the saponification test is made.

**mmonia or Soda.**—From 7 to 10 grams of the oil are dissolved
e ether and the solution extracted four successive times with dilute
acid (1 part of conc. acid and 6 parts of water). The acid liquids
distilled with excess of caustic soda—when ammonium sulphori-
concerned—and the ammonia absorbed in standard acid; with
sulphoricinate, the acid liquors are evaporated to dryness and the
ighed as sulphate.

**on.**—The oil is shaken with dilute sulphuric acid and a few drops
sium ferrocyanide solution, ether being then added and the liquid
aken and then left to stand. If iron is present, a more or less interse
appears at the zone of contact of the two liquids.

⁂

Turkey-red oils, prepared from castor oil, usually contain 45–60%
atty substance (the rest being water), but there are more concentrated
th 85–90% of fat (double oils). Those with about 45% of fat have
fic gravity 1·017–1·035 at 15°. The greater part of the fat consists
ble sulpho-acids and a small part of soluble sulpho-acids; neutral fat
t only in small proportion (1–2%). No iron should be present.

## OLEINE

### (Oleic Acid)

consists of the liquid fatty acids (mainly oleic acid)—more or less
ely separated from the solid acids—yielded by animal tallow, bone
etable tallow, palm oil and other fats. According to its method of
tion, it is distinguished as *oleine of saponification* and *distillation*
the latter, unlike the former, usually contains a large proportion
ocarbons resulting from the method of its preparation). In either
s a brownish-yellow or brownish-red liquid, with a peculiar odour,
luble in 85% alcohol, acetic acid or petroleum ether.

most important determination to be made in commercial oleines
following:

**Acid, Saponification, Ester and Iodine Numbers.**—These are
ned by the ordinary methods already described in the preceding

To separate and estimate the unsaponifiable substances, indicated on p. 388 are used.

To ascertain if the unsaponifiable matter is composed c carbons naturally occurring in distillation oleine or of added m rotatory power and the iodine number of the unsaponifiabl determined: in the former case the value of $[\alpha]_D$ is from + 4 and the iodine number 62–69, whereas mineral oils have p rotatory power or iodine number.

**3. Determination of the Solid Fatty Acids (Palmitic a** —This may be effected by the methods indicated in the prec (p. 384) or by determining the *solidifying point of the oleine* ( chapter, p. 418). From the point of solidification obtained, of stearine is deduced by means of de Schepper and Geitel's has been prepared with the aid of mixtures of pure oleine wi point 5·4° and stearine with solidifying point 48°:

TABLE L

**Content of Stearine in Oleine**

| Solidifying Point (° C.). | Percentage of Stearine (48°). | Solidifying Point (° C.). | Percentage of Stearine (48°). | Solidifying Point (° C.). |
|---|---|---|---|---|
| 6 | 0·3 | 15 | 6·6 | 23 |
| 7 | 0·8 | 16 | 7·7 | 24 |
| 8 | 1·2 | 17 | 8·8 | 25 |
| 9 | 1·7 | 18 | 9·8 | 26 |
| 10 | 2·5 | 19 | 11·2 | 27 |
| 11 | 3·2 | 20 | 12·1 | 28 |
| 12 | 3·8 | 21 | 13·2 | 29 |
| 13 | 4·7 | 22 | 14·5 | 30 |
| 14 | 5·6 | | | |

⁂

A good oleine should have an acid number about 179, corre about 90% of free fatty acids, calculated as oleic acid. Oleine found with 80–98% of free acids.

The content of neutral fat may vary from 0 to 20% (usuall

The iodine number is usually 80–90. If it exceeds 90, the pres linolenic and other less saturated acids derived from drying ve indicated.

The unsaponifiable substances should not exceed 2% in saponi but may reach 10% in distillation oleine.

## WOOL FAT OLEINE

is the liquid part of distilled wool fat, consisting of free fatty acids 5), hydrocarbons and a little cholesterol and isocholesterol.

a more or less turbid liquid of a reddish-brown colour and more uorescent and with a peculiar odour recalling that of wool fat. It e in 95% alcohol, ether, benzine, etc.

conc. sulphuric acid, its chloroform solution gives a red coloration een fluorescence (cholesterol). It may be adulterated with mineral oils or resin.

nalysis includes the following:

**cid and Saponification Numbers and Unsaponifiable Matter.** made of the methods described in the preceding chapter (General , 7 and 19).

**lineral and Resin Oils.**—From 50 grams or more of the oleine ponifiable substances are extracted by the ordinary methods, and ecific gravity, index of refraction, rotatory power (in about 3–4% solution and in a tube 10 cm. long at a temperature of 18–20°) ne number determined.

presence of mineral oil may be presumed when these unsaponifiable es have very low rotatory power and iodine number. The presence oil may be recognised by the specific gravity being greater than d the refractive index above 1·51.

**esin.** The soap solution remaining after the separation of the ifiable matter is decomposed with an acid and the fatty acids then y means of Morawski's reaction (*see* preceding chapter: General , 20).

s quantitative determination Twitchell's method (*ibid.*) is followed.

e applying Morawski's reaction, it is necessary thoroughly to separate ponifiable matter in order to remove the cholesterol, which gives a eaction.

⁂

wool fat oleine should not contain more than 60% of unsaponifiable es. These are liquid and have approximately the appearance of mineral ey should, however, have: $D = 0{\cdot}900$–$0{\cdot}917$; refractive index (at = 1·49–1·51; $[\alpha]_D = +15°$ at least (in exceptional cases as low as iodine number = 50–80.

## STEARINE

### (Stearic Acid)

to the feel and soluble in alcohol, especially in the hot.

Analysis of commercial stearines comprises principally the

**1. Solidifying Point (Titer).**—This is determined by Dalic (*see* p. 418), the content of stearine being deduced by means sponding table; when, however, fatty acids alone are co number given in the table is multiplied by $\frac{100}{95}$ (*see* p. 419).

**2. Acid, Saponification and Iodine Numbers.**—By given in the preceding chapter.

The iodine number depends on the quantity of oleic acid of iso-oleic acid) in the stearine and this may be calculated fro number by means of the formula

$$O = \frac{100}{90,} \times I, \text{ or } O = 1{\cdot}11 \times I,$$

where O = oleic acid sought I = iodine number of the stea is the iodine number of pure oleic acid.

**3. Detection of Various Extraneous Substances.**– stearines sometimes contain solid paraffin or ceresine, wool fat and carnauba wax. The presence of such substances may be a rule when the acid number of the stearine is less than 195, proved definitely as follows:

(*a*) A few grams of the stearine are digested in the hot with If the substance does not dissolve completely, the liquid is all and filtered and an examination made of the insoluble part. may contain solid paraffin or ceresine, beeswax or carnaub presence being indicated by the melting point, the acid and s numbers, etc. (*see* articles on Paraffin Wax, Ceresine and B

(*b*) A quantity of the stearine is hydrolysed with alcoholic p unsaponifiable substances extracted and examined by the meth on p. 388 *et seq.*; the presence of cholesterol will indicate th wool fat stearine in the substance.

If then it is necessary to determine the various acids compos (stearic, palmitic, oleic) and to test for stearolactone, the meth in the preceding chapter (*see* pp. 384 and 383) may be foll

Finally, when the presence of lactones is excluded, that c may be deduced from the ester number and may be confirm for glycerine (*see* p. 384).

⁂

Commercial stearines usually solidify between 48 and 55° (*ti* for saponification stearine being somewhat higher than that f

## WOOL FAT STEARINE

is the solid part of distilled wool fat and consists of fatty acids and
ifiable substances (hydrocarbons, cholesterol).

rding to the consistency, it is distinguished as *Soft stearine*, melting
5°, and *Hard stearine* or *Wool fat wax*, melting above 45°.

eneral, these products have a waxy appearance, a yellow or brownish
nd a pronounced odour of wool fat, and they are soluble in hot
and in ether, benzene or chloroform. When treated with conc.
c acid, the chloroform solution turns red and afterwards violet
green fluorescence (cholesterol).

lysis of wool fat stearine includes determinations of the melting
cid number and content of unsaponifiable substances, as well as
r added hydrocarbons (vaseline, paraffin wax) or resin.

**aseline or Paraffin Wax.**—The unsaponifiable substances from
s of the stearine are boiled for 2 hours in a reflux apparatus with
their weight of acetic anhydride. The product is then washed
ly with boiling water until the reaction is neutral and in one part
yl number is determined (*see* p. 378). Another part (about 5
is boiled with 50 c.c. of 90% alcohol, the liquid being filtered off
residue boiled with 40 c.c. and then with 30 c.c. of 90% alcohol.
part insoluble in alcohol, which consists of hydrocarbons alone, the
gravity, rotatory power (in benzene solution at about 20°) and
umber are determined.

**esin.**—This is tested for as in wool fat oleine (*see* p. 451).

⁂

rding to Marcusson and Skopnik[1] and to Coen,[2] wool fat stearines
t between 40° and 65°; they contain 56–90% of free acids (calculated as
cid) and 9–42% of unsaponifiable substances, which are brown, fluores-
sty or semi-liquid masses with a faint aromatic odour and have the
umber about 25–37, the $[\alpha]_D$ + 12° to + 30° and the iodine number

portion of the unsaponifiable matter which does not combine with
nhydride (hydrocarbons free from higher alcohols) has D = 0·907–
$]_D$ = + 12° to + 21°, and iodine number = 26–54.

tion of extraneous hydrocarbons may be suspected when the acetyl
of the unsaponifiable substances is less than 25 and the portion of them
binable with acetic anhydride has a specific gravity less than 0·9, $[\alpha]_D$
n + 12° and an iodine number less than 26.

proportions of mineral substances (soda, lime, sulphates) a residues (hide, membranous fragments) resulting from the preparation.

This product forms a fairly dense, almost pasty, yellow or or which has a special odour recalling that of fish oil and remains h even on long standing.

*Artificial dégras* is obtained by mixing natural dégras with f or resin oil, vaseline, wool fat, tallow, etc., or by artificial oxida oils, followed by emulsification with water and sometimes by the other extraneous substances mentioned above.

Artificial dégras is also a yellow or orange dense liquid, whic more liquid than the natural product and has a peculiar fish on long standing, it tends to divide into two layers, the wate the bottom.

Analysis of dégras includes various determinations and te as a guide in ascertaining if it is a natural or artificial product, that is, based solely on fish oils, or if it is mixed with tallow, wool oils, vaseline or resin oils, these being the most frequent dégras.

The principal determinations are as follows :

**1. Water.**—10 grams of the dégras are placed in a por previously heated to redness with about 10 grams of coarse and tared ; the fat is mixed well with the sand and the dish a dried at 120° until of constant weight (4–5 hours). The los gives the water.

**2. Non-fatty Substances (Organic Residues).**—20 gra dégras are dried in an oven at 120° or even over a direct liquid being stirred with a thermometer and care taken that its does not exceed 105° ; the dried product is dissolved in petr and the solution filtered through a tared filter, the insoluble m washed with petroleum ether and then with a little ether or alcohol, dried at 100° and weighed.

This insoluble matter consists principally of epidermis and h readily recognisable with a lens or microscope, together with impurities.

On the other hand, evaporation of the petroleum solution a of the residue dried at 105° gives the total fat ; the latter is determinations indicated under 4 (below).

**3. Ash.**—10 grams of the dégras are carefully heated in dish over a naked flame until copious fumes are emitted, the then heated more strongly on a sand-bath and finally in a muff ation of the non-fatty sub-

2).. From the acid number the percentage of free acids expressed acid (*see* p. 374) is calculated.

**gragene.**—This is the special resinous substance formed by the of the fish or blubber oils [1] and is what gives *body* to the dégras, its power of emulsivity with water and renders it specially adapted eatment of skins. It is determined as follows [2]:

ms of the dégras, either as it stands or after drying at 100° as under 2 (above), are dissolved together with 7 grams of caustic c.c. of water and 50 c.c. of alcohol, the solution being heated on ath in a reflux apparatus until saponification is complete (about The alcohol is then expelled, the soap dissolved in water and vith hydrochloric acid, and the whole boiled until the mixture of ls and dégragène becomes quite fluid. When cool, the mass is l to a separating funnel and the flask rinsed out with about 150 troleum ether boiling below 75°; the whole is well shaken and stand until the aqueous acid liquid separates sharply from the solution, the former being then run off. The funnel then con- etroleum ether solution of the fatty acids and of the unsaponifiable s of the dégras, together with an insoluble, blackish, resinous tituting the dégragène, which adheres well to the walls ot the that the petroleum solution may be poured from the top of the thout any of the dégragène being lost. The dégragène is then th a little petroleum ether and dissolved in hot alcohol, the solu- filtered if necessary, the alcohol evaporated and the residue 00–105° and weighed.

**saponifiable Substances.**—According to Baldracco,[3] these etermined exactly as follows: 15–20 grams of the dégras are by boiling with 5 grams of caustic potash dissolved in 10 c.c. nd 50 c.c. of alcohol for 2–2½ hours in a reflux apparatus, the g then transferred to a dish and the alcohol completely expelled ation on a water-bath. The residue is well mixed with 8 grams bicarbonate and 50–60 grams of coarse quartz sand previously d calcined, and completely dried in an oven at 110°. The mass oken into small pieces, placed in an extraction thimble and ex- th petroleum ether boiling below 75°.

roleum solution is washed several times with water in a separating then evaporated, the residue, when dried at 110° and weighed, g the unsaponifiable matter contained in the dégras.

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rgest proportions of dégragêne are furnished by whale oil and cod-liver oil,

resin oils in the way indicated on p.
contains wool fat, mineral oils and other unsaponifiable matt

⁂

Good dégras is golden-yellow or orange and homogeneous and

Natural dégras usually contains 15–25% of *water*, while the a
ducts contain 10–25%.

The other components may vary within the following limit
*referred to the dry dégras* (free from water):

The *non-fats* (various organic residues) may reach 8% in na
(ordinarily 2–5%), but are less than 1% in artificial dégras.

The *ash* may amount to 5% with natural dégras, but is less
the artificial product; it should contain only traces of iron (no
0·05% of the original dégras).

The *free fatty acids*, calculated as oleic acid, may vary from
natural dégras, but are usually less than 20% in the artificial d

The *saponification number* is above 200 (220–240) in natura
not less than 190 in artificial dégras. A value less than 190 (re
dry substance) denotes the presence of extraneous matter, such
resin oils, vaseline or wool fat.

The proportion of *dégragène* is somewhat variable, since it de
mode of preparation of the dégras. Usually natural dégras con
and the artificial product not more than 10% of dégragène.

The *unsaponifiable matter* does not exceed 3% in pure dégras, wh
or artificial, but is considerably higher in products adulterated
or resin oils, vaseline or wool fat.

## CANDLES

Three types of candles are usually sold: stearine, paraffi

*Stearine candles*, which are opaque and white, should be
stearine (mixture of stearic and palmitic acids, etc.; *see* S
very often they contain a certain quantity of paraffin wax
and sometimes ceresine or a small quantity of carnauba wax
melting point).

*Paraffin candles*, which are translucent and white, are made
wax with a high melting point (about 50°), usually with th
3–15% or even more (up to about 33%) of stearine, such be
*composite candles*.

*Wax candles*, which are yellowish and opaque and posses
teristic odour of wax, should be made from pure beeswax,
nowadays usually made from mixtures of wax, paraffin wax,
stearine, the wax being present often in small amount.

Analysis of candles is usually made with the object of det
composition, but includes also tests of the illuminating power

the quantitative determinations it is well to melt a whole candle st various pieces taken from several candles at different points in obtain a homogeneous and representative sample.

further necessary to determine the weight of the *wick*, several eing broken from one or more candles and weighed and the wick efully separated and weighed: the weight of the wick is referred arts of candle.

commonest cases of analysis of candles are the following:

IXED STEARINE AND PARAFFIN (OR CERESINE) CANDLES. About s of the sample are heated and shaken with 50 c.c. of 90% alcohol water-bath, the liquid being subsequently titrated with decinormal m hydroxide in presence of phenolphthalein: 1 c.c. N/10-KOH = am of stearine (mean molecular weight of ordinary stearine = 270). liquid is then again heated on the water-bath for about an hour, quent shaking, with 4–5 c.c. of concentrated potassium hydroxide to saponify the small quantity of neutral fat or any lactones present tearine (for greater precision the saponification number also may rmined). The solution is then diluted with water and allowed to til the paraffin is thoroughly solidified to a *solid disc*, the aqueous eing then decanted off and the paraffin washed several times with being heated and cooled each time. The washed paraffin is finally d into a dish, dried in an oven at 105° and weighed.

paraffin thus separated is then tested for ceresine by the methods n p. 364.

stearic acid (stearine) calculated from the acid number and the weighed directly are then referred to 100 parts of candle, allowance ade for the weight of the wick (*see* example given below for case *b*). rapid, approximate determinations it is sufficient to calculate the acid from the acid number and the paraffin by difference.

IXED WAX, STEARINE AND PARAFFIN CANDLES. In these candles be necessary to calculate either all three of the components or only affin (or ceresine).

*etermination of all of the components.* The acid and saponification s are determined in the usual way, the various components being lculated as in the following example.

AMPLE: The wick of a candle is found to represent 0·4% of the weight candle, while the wick-free mass has:

Acid number = 77·0
Saponification ,, = 84·7,

Ester number = 7·7.

the mean saponification

$$100 : 95 = 10{\cdot}26 : y,$$

so that

$$y = 9{\cdot}75.$$

This number $y$ is deducted from the saponification number found stance,

$$84{\cdot}7 - 9{\cdot}75 = 74{\cdot}95,$$

and from this the stearic acid ($z$) is deduced from the proportion

$$207 : 100 = 74{\cdot}95 : z,$$

so that,

$$z = 36{\cdot}11\% \text{ of } \textit{stearic acid}.$$

(*c*) The solid paraffin is then given by difference,

$$100 - (10{\cdot}26 + 36{\cdot}11) = 53{\cdot}63\% \text{ of } \textit{paraffin}.$$

(*d*) The composition of the entire candle (with the wick) is th

| | |
|---|---|
| Wick | 0·40 |
| Wax | 10·22 |
| Stearic acid | 35·96 |
| Paraffin | 53·42 |

2. *Determination of the paraffin* (*or ceresine*) *alone*. In this cas of the candle are boiled for 3–4 hours with alcoholic potash in a with a long tube to act as reflux condenser and then left to coo paraffin has set well at the surface of the liquid. The latter is t off together with all the unsaponifiable matters of the wax wh suspended in a flocculent form, care being taken that the wl paraffin remains in the flask. The paraffin is then again boiled f with alcoholic potash, the whole being afterwards transferred hot to a separating funnel, the flask being rinsed out with bo so as to obtain all the paraffin in the funnel. The aqueous alcol is run away and the paraffin remaining in the funnel washed se with hot water and subsequently rinsed out into a small beake help of very hot water. After cooling, the solid paraffin disc 100–105° in a tared dish and weighed.

This paraffin is then tested for ceresine by the methods gi Paraffin wax and Ceresine.

**2. Illuminating Power.**—This is measured as with petr Chapter VIII, Lighting Oil, 7).

**3. Bending Test.**—This test, made especially with paraff consists in introducing the base of the candle into a suitable supp the candle is horizontal and leaving it in a room at a constant te of 22–25° for some hours to ascertain if it becomes curved and what extent. A standard candle is used for purposes of compa

acids. Such
e neutral or only slightly alkaline, and this group includes, for toilet soaps in general, so-called Marseilles white soap and certain oaps.

lled "*cold*" soaps, obtained by saponifying fats with an alkaline out adding common salt, are usually very alkaline; they contain rine and all the impurities of the fats and alkali used. Potash long to this class.

are analysed to ascertain their composition and to see if they d to definite uses. Analysis includes mainly determinations of r, total fat, alkali, resin, glycerine, etc.

**mpling.** The various determinations require at least 100 grams which is stored in a well-dried and closed glass jar.

soap in small pieces or cakes, these are cut into at least four parts se and crosswise), from which thin shavings are taken and cut the whole being thoroughly mixed and a portion taken for analysis.

soap in blocks or large rectangular pieces, two triangular prisms r bases on two opposite sides are taken so as to represent proportion the dried outer part and the more hydrated inner part; these e rapidly cut up, well mixed and the sample to be analysed then

r powdered soaps are well mixed with a spatula or in a mortar and le then taken.

**ater.**—In a platinum dish, tared with a glass rod, 5–8 grams of are weighed, the dish being then heated in an oven first at 60–70° at 100–105° until of constant weight, the mass being stirred from time with the rod. Loss of weight represents water.

ft soaps or others containing a large proportion of water, a certain of siliceous sand or ground pumice, previously ignited, is tared sh with the glass rod.[1]

**tal Fat.**—20 grams of the soap, dissolved in water, are sed by excess of dilute sulphuric acid (1 : 3) or of normal sulphuric *also* 4), the solution shaken with 100 c.c. of petroleum ether, b.pt. e 65°, and the acid liquid separated and again shaken with 100 troleum ether. The two petroleum extracts are united, washed er, filtered (if necessary) into a tared dish and evaporated at a erature, the residue being dried in an oven at about 110° to constant

gives the total fat, which, besides the fatty acids and resin acids ng normal soap, may contain also neutral fat and unsaponifiable s; it is therefore examined further (*see* below: 5, 8 and 11).

utilised for the determination of the alkalies (*see* 4).

**4. Total Alkalies**:—This determination may be combine preceding one of the total fat. For this purpose it is sufficient to the aqueous solution of 20 grams of the soap with 100 c.c. of norma acid and then to proceed as in 3, care being taken to lose no aqueous acid liquid separated from the petroleum ether solut

This liquid, collected quantitatively in a conical flask, is ti normal potassium hydroxide solution in presence of methyl ora

The difference between the volume of normal acid added solution and the volume of normal alkali necessary to neutralise ing free acid, represents the total alkali—existing as hydroxides, silicates, borates and soaps—in the soap. This is expressed oxide for hard or powdered soap, and as potassium oxide for 1 c.c. normal $H_2SO_4$ = 0·031 gram of $Na_2O$ = 0·047 gram of

**5. Alkalies combined with Fatty Acids.**—The alkalies with fatty (or resin) acids, that is, as soaps, are deduced fro number of the total fat obtained as in 3.

The acid number is determined as on p. 374, and the results a as $Na_2O$ for hard or powdered soap and as $K_2O$ for soft soa

**6. Free Alkalies.**—The presence of excess of alkali in a soap (1) by dissolving 1 part of the soap in 50 parts of 95% alcohol a few drops of phenolphthalein solution (red coloration), or (2) on to a section of the soap, recently cut, a drop of mercuric chlor (yellow coloration) or mercurous nitrate solution (black color

Quantitatively free alkalies as hydroxide and as carbonat mined as follows:

(*a*) ALKALIES AS HYDROXIDE. A solution of 10–15 grams o glycerine in 100 c.c. of absolute alcohol is neutralised, if necess few drops of alcoholic potash (phenolphthalein as indicator of the soap are then dissolved in it and 2–5 c.c. of cold, saturat strontium chloride solution added to precipitate the alkali carb free alkalinity being then titrated with standard alcoholic stea tion in presence of phenolphthalein.[1]

(*b*) ALKALIES AS CARBONATE. If the soap does not conta borates or other alkaline salts, the alkalies as carbonate may b *indirectly* or *by difference*, by subtracting from the total alkali sum of the alkali as hydroxides and that combined with the (*see* 5 and 6*a*), all expressed as $Na_2O$ or $K_2O$: this difference into $Na_2CO_3$ or $K_2CO_3$, represents alkalies as carbonates.

When silicates, borates or other alkaline salts are present, t

**ee Fatty Acids.**—These are determined only when the soap does it an alkaline reaction.

ms of the soap are dissolved in neutral 60% alcohol and the itrated with alcoholic decinormal caustic potash in presence of halein. The acidity is expressed as oleic acid: 1 c.c. N/10-KOH gram of oleic acid.

**utral Fat and Unsaponifiable Substances.**—From 6 to 8 the total fat, extracted as in 3, are dissolved in about 50 c.c. of iol and the liquid neutralised with seminormal alcoholic caustic presence of phenolphthalein (to a faint pink coloration); it is ted with about 50 c.c. of water and extracted successively with 0 c.c., and 50 c.c. of petroleum ether (b.pt. not above 65°). The roleum ether solutions are washed three times with three quantities c.c. of 58% alcohol and then evaporated, the residue being dried 5° and weighed.

ives the neutral fat plus any unsaponifiable substances contained p.

sence of the latter (which may be detected by a separate test), ed residue must be saponified with alcoholic potash, the solution with petroleum ether in the manner described above, and the ct, representing the unsaponifiable substances, weighed. The t is then given by difference.

**sin.**—The presence of resin (colophony) in a soap is readily y the application of Morawski's reaction (*see* p. 390) to the fatty ined from the soap itself, provided the latter does not contain in which case the test is made on the fatty acids after elimination nsaponifiable matter.

antitative determination of the resin is effected by Twitchell's *see* p. 390)

**lycerine.**—This occurs in "cold" soaps and in soft or potash 5%), in which its presence is due to the method of preparation, n transparent or glycerine soaps, to which it is purposely added.

s determination, 20–25 grams of the soap are dissolved in hot composed by means of dilute sulphuric acid and filtered to remove acids. The filtrate is neutralised, defecated with lead acetate, o a definite volume and filtered, the glycerine being estimated in t part by the dichromate method (*see* Glycerine).

soap contains ethereal oils, sugar, dextrin or other substance by dichromate, this method is inapplicable. In such cases the aqueous liquid is evaporated with addition of lim nd the glycerine may contain resin and palm oil, and green or brown ones, s oil and resin. Further, the solidifying point, acid and iodi and certain colour reactions and other investigations of the obtained from a soap give information, up to a certain point, acter of the fats used.

For example: Soaps prepared from oleine give fatty acids w at a low temperature and contain only small quantities of sol examination of these, *see* p. 384).

Soaps from coco-nut oil give fatty acids with an acid numb and a low iodine number.

Those from linseed and other drying oils contain hydroxy-ac in the cold in petroleum ether and yield fatty acids with a number.

Soaps from cottonseed, sesamé and arachis oils give fatty show Milliau's and Villavecchia and Fabris' reactions and cont acid (*see* Cottonseed, Sesamé and Arachis Oils, preceding cha

Resin soaps give the reaction for resin with acetic anhydr phuric acid (*see* 9).

Tests for cholesterol and phytosterol (*see* Hog's Fat) sho soap contains animal or vegetable fats.

**12. Extraneous Substances.**—These may be of vari and principally as follows:

(*a*) MINERAL SUBSTANCES. Alkaline chlorides, sulphates, and phosphates, water glass, borax, heavy spar, kaolin, talc, si pumice, tripoli, etc. Some soaps (especially powdered) contain a agents, such as sodium peroxide, perborates, percarbonates and

All these substances may be recognised and determined the soap with absolute alcohol and examining the insoluble re ordinary analytical methods, both qualitative and quantitati

(*b*) VARIOUS ORGANIC SUBSTANCES. These may consist of dextrin, sugars (saccharose, glucose, molasses), vegetable g and casein. Such substances also remain undissolved when treated with absolute alcohol and may be detected in the resid of the microscope, by treating with iodine (starch, dextrin), by and reducing powers (sugars), by the way in which they bu etc.).

(*c*) ALCOHOL. About 50 grams of the soap are dissolved i tepid water and decomposed with a slight excess of dilute s and filtered. The filtrate (which should not be much more tha neutralised with potash and distilled, 100 c.c. of distillate bei identify nitrobenzene, the ethereal extract obtained in the above r is dissolved in a little alcohol and a scrap of zinc and 2–3 c.c. of sulphuric acid added to the solution. After 2–3 hours the liquid is l into a dish and the filtrate exposed for an instant to chlorine issuing test-tube containing a little potassium chlorate and conc. hydro- acid : a persistent violet coloration is produced (*Armani and Barboni*).

ps based on coco-nut or palm oil give, with steam, a small quantity of e acids of peculiar odour, which must not be confused with that of soap ing added perfume.

MEDICINAL SUBSTANCES. Medicinal soaps are made with the most substances, mostly antiseptics, among which are formalin, phenol, alene, tar, ichthyol, camphor, sulphur, salicylic and boric acids, ry salts, arsenical compounds, juices of medicinal herbs, etc.

ese may be tested for by shaking the soap with ether, evaporating hereal solution and examining the residue by suitable methods, or solving the soap in water, precipitating with barium chloride and g the barium soap thus formed with alcohol or ether.

rcury and arsenic compounds, boric acid and the like may be detected composing the soap with hydrochloric or nitric acid and then testing id aqueous liquid.

e of the commonest medicinal soaps contains carbolic acid. To ine the proportion of the phenol, 5–10 grams of the soap are dissolved er with addition of caustic soda, the solution shaken with ether and ueous liquid treated with excess of sodium chloride to precipitate ole of the soap. The liquid is then filtered and the insoluble residue d with saturated sodium chloride solution, the liquid being then ed with dilute sulphuric acid and the phenol estimated by means of ne (*see* Carbolic Acid, p. 330).

MINERAL AND RESIN OILS, PARAFFIN WAX, TURPENTINE, ETC. may be detected by extraction of the soap with ether. In most mixtures of soap with mineral or resin oils, vaseline and the like, ute lubricants or cart-grease, analysis of which is dealt with in the on Lubricants (*see* p. 365).

## GLYCERINE

*ude glycerine* (*saponification*, *soap-lye* or *distillation glycerine*) forms a wish or brown liquid with a repellent odour and an acrid taste, while *ed glycerine* (*refined*, *distilled* or *double distilled*, *for dynamite*) consists olourless or almost colourless, odourless, syrupy liquid with a sweet salts (chlorides, sulphates, sulphides, sulphites, thiosulphates, li and organic substances (soaps, tarry substances, proteins, et analysis is usually restricted to determinations of the alkali (fre bined), free acid, residue on evaporation, water and glycerine.

**Sampling.**—The sample should contain portions from ev forming the parcel and should be taken, if possible, as soon as filled, since crude glycerine often contains suspended matters gradually deposited.

If such deposition has already occurred, a good average sa be obtained with the help of a special sampler.[2]

Note is made of any suspended matter observed while the being taken, and also of the temperature and of the form and c the vessels when these are not similar.

**1. Ash and Total Alkali.**—From 2 to 5 grams of the gly weighed in a platinum dish and evaporated carefully over a d and the residue charred at the lowest possible temperature.

The carbonaceous mass is then extracted with boiling wat and washed. The filter and the contained charred mass are in the same dish, the aqueous extract and wash-waters being the whole evaporated to dryness on a water-bath and again ignite so that the ash does not fuse.

The ash thus obtained is weighed and then dissolved in water a with normal acid (indicator : methyl orange), the alkalinity being as percentage of $Na_2O$ in the glycerine.

**2. Free Caustic Alkali.**—20 grams of the glycerine are a 100 c.c. flask, dissolved in 50 c.c. of recently boiled water, tr excess of barium chloride solution and 1 c.c. of alcoholic phen solution, made up to volume with boiled water, shaken vigorous at rest. Subsequently 50 c.c. of the clear liquid are pipetted off a with normal acid. The free alkali is calculated as $Na_2O$ per 1 glycerine.

**3. Alkali as Carbonate.**—10 grams of the sample are di 50 c.c. of distilled water, treated with sufficient normal acid to the total alkali (*see* 1) and boiled in a reflux apparatus for 15– The condenser is washed down with recently boiled distilled wat free acid titrated with normal soda in presence of phenolphtha

The result is calculated as percentage of $Na_2O$ and from this

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[1] The methods were fixed in 1911 by an International Commission English, German and French analysts, as a result of the Congress of Gly facturers held in London in 1909.

**:y.**—Ten grams of the sample, dissolved in 50 c.c. of recently are titrated with normal caustic soda in presence of phenolph- e result is expressed as $Na_2O$ necessary to neutralise the acidity s of the glycerine.

**ue at 160°.**—In a 100 c.c. measuring flask, 10 grams of the weighed, diluted with a little water and treated with normal i (according as the sample is alkaline or acid) in such amount erine assumes an alkalinity corresponding with 0·2% of $Na_2O$. then made up to volume and shaken, 10 c.c. (or, if the sample re, a lesser quantity sufficient to give a residue not exceeding ams) being transferred to a tared porcelain dish 12 mm. deep at base 6 cm. in diameter. The bulk of the water is evaporated ter-bath and the dish then placed in an air-oven (30 × 30 × 30 is furnished with a thermometer, rests on an iron plate 20 mm. as half-way up a shelf covered with asbestos board on which containing the glycerine rests. The latter is heated at 160° aces of thin vapour are emitted, then removed from the oven, ool, 0·5–1 c.c. of water added and the contents gently mixed. again evaporated on the water-bath and subsequently on the ° until the residue, placed within the oven, no longer froths. on usually requires 2–3 hours.

int the dish is kept in the oven at 160° for exactly one hour, removed, allowed to cool in a desiccator over sulphuric acid The residue is next treated with water, re-evaporated, dried, for an hour as before, this procedure being repeated until the ed does not exceed 1–1·5 mgrms. per hour.

ht of the residue at 160° is *corrected* for the acid or alkali added alkalinity to the desired point. With acid glycerine, 0·022 tracted for each c.c. of normal alkali added. With alkaline e correction applied is that resulting from the transformation d $Na_2CO_3$ into NaCl. The corrected weight gives the residue is calculated for 100 grams of the glycerine.

due is kept for the determination of any impurities capable of

**nic Residue.**—The organic residue represents the difference e residue at 160° and the ash.

l, however, be noted that the $CO_2$ formed for the transformation acids during the incineration is not contained in the organic

**er.**—On a clock-glass of about 15 c.c. capacity are placed 2–3 again, the glass is left in the desiccator at the above pressure weight is constant (usually about 48 hours at 15° are required). of weight represents water.

**9. Glycerine.**—Either of two methods may be used[1]:

*A.* ACETYLATION METHOD, applicable to crude glycerine, pr contains not more than 50% of water.

*Reagents* required:

(a) *Acetic anhydride* (puriss.), which should be carefully exa to purity and which in a blank esterification experiment should n more than 0·1–0·2 c.c. of normal soda, and which should turn onl brown when boiled for an hour with sodium acetate.

(b) *Pure dry sodium acetate,* obtained by fusing the salt in a dish, powdering it rapidly and storing in a closed vessel in a d It should be absolutely free from moisture.

(c) *Normal caustic soda solution,* which should be very care pared with well-boiled water and should be quite free from ca

(d) *Normal sulphuric acid.*

(e) *Phenolphthalein solution,* containing 0·5 part in 100 parts and neutralised.

*Procedure.* In a round-bottomed flask of about 120 c.c. capa washed and dried, 1·25–1·50 gram of the glycerine is rapidly w grams of the sodium acetate and 7·5 c.c. of acetic anhydride bei The flask is then connected with a small reflux condenser by m ground joint or a rubber stopper (the latter should be first pu exposure to the vapour of boiling acetic anhydride) and the liqu gently for about an hour. It is then cooled somewhat and 50 c.c. o boiled hot water (at about 80°) added by way of the condenser liquid being shaken and heated, if necessary—but not above 8 solution is complete (excepting for a few black flocks due to im The condenser tube is washed down with a little boiled water, detached and the stopper or ground joint also washed down. The filtered into a flask holding about a litre, the original flask and fil thoroughly washed with boiled, cold water. 2 c.c. of phenol solution are next added and the liquid neutralised with the norm soda solution (to a faint yellowish-red coloration), care being shake the flask continually while the alkaline solution is run i burette.

After the neutral point is reached, a further quantity of 50 c.c. caustic soda is added, the flask being then closed with a stopper by a long glass tube to act as reflux condenser, and the liquid boil ith *crude soap-lye glycerine,* when this contains more than 2·5% of ic residue at 160° (*see* 7), the residue at 160° obtained as in 6 (above) also be acetylated in the manner just described; if the result thus ned corresponds with more than 0·5% of glycerine (on the residue , the excess over 0·5% is deducted from the percentage of glycerine in the sample itself.

or *distilled saponification glycerine* and the like, acetylation of the ic residue is carried out when this exceeds 1%, the procedure being fore and account being taken only of the excess of glycerine over 0·5%.

DICHROMATE METHOD. *Reagents* required:

) *Potassium dichromate* (puriss.), powdered, dried at 110–120° and in a well-closed vessel.

) *Standard dichromate solution*: 7·4564 grams of dichromate (*a*) are ved in water to 1 litre.

) *Ferrous ammonium sulphate,* to be titrated with the dichromate lows: 3·7282 grams of the dichromate are dissolved in 50 c.c. of water 50 c.c. of dilute sulphuric acid (*g*). A convenient excess of ferrous onium sulphate (e.g., 3–4 grams), accurately weighed, is then added he excess determined by means of the dichromate solution (*b*), a drop e liquid being removed from time to time and tested with potassium yanide. The amount of dichromate corresponding with 1 gram of ferrous ammonium sulphate is then calculated (with pure products m of the sulphate = 1·25 gram of the dichromate).

l) *Silver carbonate,* to be prepared afresh for each operation by treating c.c. of 0·5% silver sulphate solution with 4·9 c.c. of normal sodium nate solution, allowing the precipitate to deposit, decanting off the l and washing once by decantation.

) *Basic lead acetate,* obtained by boiling 10% neutral lead acetate ion with excess of litharge for an hour and filtering while hot.

) *Potassium ferricyanide* in 0·1% solution.

g) *Dilute sulphuric acid,* conc. acid being mixed with its own volume ater.

*rocedure.* 20 grams of the sample are made up to 250 c.c. with r in a 250 c.c. flask. Of this solution, 25 c.c. are treated, in a 100 c.c. , with the silver carbonate (*d*) and, after about 10 minutes, with 5 c.c. e lead acetate (*e*), the liquid being then made up to the mark and 1·5 of extra water added to compensate for the volume of the precipitate. whole is then shaken vigorously and filtered through a dry filter, the 10 c.c. of filtrate being discarded and the remainder refiltered if turbid.[1] nall portion is tested to ascertain if fresh addition of the lead acetate

dichromate and sulphuric acid) with 12 drops of
(1 : 4) to precipitate the excess of lead and then with 3·7282 grar
powdered dichromate (*a*) and 25 c.c. of water. When the dichr
dissolved, 50 c.c. of the dilute sulphuric acid (*g*) are added and tl
kept in a boiling water-bath for two hours, care being taken to
from organic vapours (alcohol, etc.) and from dust. It is then a
cool, an exactly weighed amount (in excess) of ferrous ammonium
(e.g., 3–4 grams) being added and the extent of the excess mea
titration with the dichromate solution (*b*), potassium ferrocyan
used, as before, as indicator.

As it is known from the titration of the ferrous ammonium
(*see c*) with how much dichromate 1 gram of the ferrous salt cor
the quantity of dichromate used in oxidising the glycerine, and
the amount of the glycerine, may be calculated : 1 gram of the di
= 0·13411 gram of glycerine.

As regards these two methods, adopted by the International Co
Tortelli and Ceccherelli [1] point out that only the second—the dichroma
—is really exact. The acetin method, according to the accurate inve
of these authors, gives inconstant and low results.

The same authors also suggest some practical modifications in the d
method.

## *B.* Pure Glycerine

With pure glycerines the specific gravity is determined anc
common impurities (heavy metals, sulphates, chlorides, oxala
arsenic, acrolein, formic acid, fats) and adulterations (sugar,
tested for. In some cases the chlorides are determined and pos
residue at 160° and other determinations described for crude
With dynamite glycerine, a nitration test is made.

**1. Specific Gravity.**—This is determined by the Westphal
picnometer or hydrometer.

If the glycerine is pure, the content of water may be calcula
the specific gravity by means of the following table (page 469).

**2. Detection of Impurities and Adulterations.**—This is
by means of the following tests :

(*a*) 1 volume of the glycerine is dissolved in 5 vols. of water
reaction of the solution tested with litmus paper : pure glyceri
be neutral.

Aliquot parts of the same solution are then treated with
sulphide and with ammonium sulphide to ascertain if *heavy m*
present (brown coloration) ; with barium chloride for

## Specific Gravity of Aqueous Glycerine

| ic gravity according to | | Percentage by weight of Glycerine. | Specific gravity according to | | Percentage by weight of Glycerine. |
|---|---|---|---|---|---|
| t 12–14°<br>t 12°=1 | Gerlach at 15° Water at 15°=1 | | Lenz at 12–14° Water at 12°=1 | Gerlach at 15° Vater at 15°=1 | |
| 691 | 1·2653 | 100 | 1·2212 | 1·2184 | 82 |
| 664 | 1·2628 | 99 | 1·2185 | 1·2157 | 81 |
| 637 | 1·2602 | 98 | 1·2159 | 1·2130 | 80 |
| 610 | 1·2577 | 97 | 1·2016 | 1·1990 | 75 |
| 584 | 1·2552 | 96 | 1·1889 | 1·1850 | 70 |
| 557 | 1·2526 | 95 | 1·1733 | 1·1711 | 65 |
| 531 | 1·2501 | 94 | 1·1582 | 1·1570 | 60 |
| 504 | 1·2476 | 93 | 1·1455 | 1·1430 | 55 |
| 478 | 1·2451 | 92 | 1·1320 | 1·1290 | 50 |
| 451 | 1·2425 | 91 | 1·1183 | 1·1155 | 45 |
| 425 | 1·2400 | 90 | 1·1045 | 1·1020 | 40 |
| 398 | 1·2373 | 89 | 1·0907 | 1·0885 | 35 |
| 372 | 1·2346 | 88 | 1·0771 | 1·0750 | 30 |
| 345 | 1·2319 | 87 | 1·0635 | 1·0620 | 25 |
| 318 | 1·2292 | 86 | 1·0498 | 1·0490 | 20 |
| 292 | 1·2265 | 85 | 1·0374 | — | 15 |
| 265 | 1·2238 | 84 | 1·0245 | 1·0245 | 10 |
| 238 | 1·2211 | 83 | 1·0123 | — | 5 |

1 c.c. of the glycerine and 1 c.c. of ammonia are heated to 60° drops of silver nitrate solution then added: the appearance of a coloration or deposit within 5 minutes denotes the presence of *acrolein* *mic acid*.

1 c.c. is heated with 1 c.c. of 15% sodium hydroxide solution: ion of ammonia indicates the presence of *ammonium* salts, or yellowing solution the presence of *glucose*. The presence of the latter may be med by boiling a few drops of the glycerine with Fehling's solution recipitate).

) 1 c.c. is heated gently with dilute sulphuric acid to ascertain if pleasant rancid odour is evolved (*fatty substances*); the liquid is then lised and boiled with Fehling's solution (*sugar*).

) 1 volume of the glycerine is treated with about 2 vols. of strong ol: turbidity denotes presence of *gum* or *dextrin*.

g) A few c.c. of the glycerine are evaporated in a small dish to ascer- f any residue remains (usually *mineral substances*).

to this are carefully dropped 20 grams of the glycerine, the beak externally cooled with water meanwhile. The product is subs transferred, with every precaution, to a graduated cylinder and no if the nitroglycerine separates promptly and if it is pale and clear. the separation of the nitroglycerine from the acid liquid is sharp, the of the former is measured ; multiplication of this volume by 1·609 gravity of nitroglycerine at 15°) gives the weight.

⁂

*Glycerine liquors* obtained directly by saponification with alkali autoclave contain 5–10 % of glycerine, whereas those resulting from sa tion by Twitchell's method or by enzymes contain 12–19 %.

*Crude glycerine* (concentrated) usually contains 80–90 % of glyce varying quantities of salts (ash), residue fixed at 160°, free acids or alka

*Refined glycerine* (pure, puriss.) should be free or almost so from the impurities already mentioned (*see* Pure Glycerine, 2).

Double distilled glycerine for pharmaceutical purposes should, in pa satisfy the various tests indicated under 2.

*Dynamite glycerine* should have a specific gravity not less than 1·26 be perfectly neutral, should contain no more than traces of chlorides (1 than 0·025 % of NaCl), sulphates, lime, magnesia, alumina and reduc stances, and not more than 0·25 % of residue fixed at 160°. In the test it should give not less than 200 % of nitroglycerine (theoretical yield, which should separate promptly as a colourless or almost colourless, clear liquid.

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